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(54) Treating metal surfaces to improve corrosion resistance

(57) Metal surfaces, particularly zinc and zinc alloy surfaces, are treated with an aqueous acidic solution containing effective amounts of

A) hydrogen ions to provide a pH of about 1.5 to about 2.2,

B) an oxidizing agent,

C) at least one of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures or cerium ions or mixtures thereof, or instead of C) iron and cobalt ions. Other treating solutions also incorporate

D) chromium ions substantially all of which are in the trivalent state, and iron ions in combination with an additional metal from C) or cerium ions, or A), B), C) and D) and F), a bath soluble and compatible silicate compound or A), B), C) and D) and G), a mixture of 1-hydroxyethylidene-1,1 diphosphonic acid and citric acid or mixtures of A), B), C) and D) with two or more of E), F) and G). The treating solution may optionally further contain halide ions and a wetting agent.

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SPECIFICATION

Chromium appearance passivate solution and pr cess

The present invention relates to passivation of metal surfaces to impart the appearance of a chromium passivate.

A variety of chromium containing aqueous solutions have heretofore been used or proposed for treating zinc, zinc alloy, cadmium, cadmium alloy and aluminium surfaces for improving the corrosion resistance properties thereof and to further enhance the appearance of such surfaces by imparting a yellow or a blue-bright coating thereto, the latter simulating a chromium finish. Such treating solutions originally contained chromium in the hexavalent state and in more recent years the chromium constituent was present as a mixture of the hexavalent and trivalent forms. The reduced toxicity of trivalent chromium and the increased simplicity and efficiency in treating waste effluents containing trivalent chromium has occasioned an increased commercial use of passivate solutions in which the chromium constituent is substantially entirely in the trivalent state. Such prior trivalent chromium passivating solutions have been found to be somewhat less effective than the traditional hexavalent chromium passivating solutions in imparting good corrosion resistance to zinc and zinc alloy, cadmium, cadmium alloy, and aluminium, aluminium alloy, magnesium and magnesium alloys surfaces and there has, accordingly, been a continuing need for further improvement in trivalent chromium passivating solutions and processes.

The excellent corrosion protection provided by hexavalent chromium passivating solutions is generally associated with a light yellow iridescent passivate film which has been recognised and embodied in ASTM specifications. Conventionally, trivalent chromium passivate films are of a clear to light-blue colour and are of inferior corrosion protection than the yellow hexavalent passivate film. This problem has been further aggravated by a conversion from conventional cyanide zinc and cadmium plating processes to acid and alkaline non-cyanide electroplating baths which produce metal deposits which are not as receptive to chromium passivate treatments.

Typical of prior art compositions and processes for treating metal surfaces are those disclosed in United States Patents Numbers 2,393,663; 2,559,878; 3,090,710; 3,553,034; 3,755,018; 3,795,549; 3,880,772; 3,932,198; 4,126,490; 4,171,231; British Patent Numbers 586,517 and 1,461,244; and German Patent No. 2,526,832.

According to its broadest aspect the present invention provides an aqueous acidic solution useful in the treatment of receptive metal substrates to impart a passivate film thereon comprising

A) hydrogen ions to provide an acidic pH;

B) an oxidizing agent; and

C) at least one of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture or cerium ions or mixtures thereof in an amount effective to impart increased corrosion resistance to the treated substrate.

The present invention is particularly applicable but not limited to the treatment of alkaline and acidic non-cyanide zinc and cadmium electrodeposits to impart improved corrosion resistance thereto. Particularly satisfactory results are obtained on decorative zinc and cadmium electrodeposits of the bright and semi-bright types although beneficial effects are also achieved on zinc and zinc alloy substrates such as galvanized substrates, zinc die castings and substrates comprised of cadmium or alloys of cadmium predominantly comprised of cadmium. While the invention in its various aspects as herein described is particularly directed to the treatment of zinc and zinc alloy surfaces, it has been observed that beneficial results are also obtained in the treatment of aluminium, aluminium alloy, magnesium and magnesium alloy surfaces to form a passivate film or coating thereon. Accordingly, the present invention in its broad sense is directed to the treatment of metal surfaces which are receptive to the formation of a passivate film thereon when contacted with the solution of the present invention in accordance with the process parameters disclosed.

In accordance with the process aspects of the present invention, zinc, cadmium, zinc alloy, cadmium alloy, aluminium and magnesium surfaces are contacted with the aqueous acidic treating solution, at a temperature ranging from about 40° up to about 150°F (4° to 66°C) for a period of time typically ranging from about 10 seconds up to about 1 minute to form the desired passivate film.

A treating bath formulation in accordance with the various aspects of the present invention which are described in detail below may be applied to a substrate to be treated by spray, immersion, flooding or the like for a period of time sufficient to form the desired passivate flim thereon. The treating solution is controlled within a temperature range of about 40° to about 150°F (4° to 66°C), with a temperature range of about 70° to about 90°F (21° to 32°C) being preferred. Temperatures above about 90°F (32°C) have a tendency to cause a rapid loss of the peroxide-typ oxidizing agents when used whereas temperatures below about 70°F (21°C) reduce the activity of the bath requiring increased contact times to achiev a passivate film of the same thickness or colour intensity as can b achieved at the higher temperatures at short time intervals. Typically, contact times of about 20 or 30 seconds to about 1 minute are satisfactorily with contact times of about 30 s conds being usually preferred.

According to a first aspect of the present invention ther is provided a passivating solution which

does not contain any chromium ions and is effective for imparting corrosion resistance to zinc, cadmium and aluminium surfaces as well as alloys thereof.

This aspect of the present invention provides a treating solution and process which is effective to selectively impart a clear blue-bright or a clear light-yellow passivate film to zinc, zinc alloy, cadmium, cadmium alloy, aluminium and magnesium surfaces which provides for improved corrosion resistance. The present invention is further characterized by a process which is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the first aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its essential constituents hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid or hydrochloric acid; an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, iron and cobalt ions in an amount effective to impart increased corrosion resistance to the treated substrate and preferably present in an amount of about 0.02 to about 1 g/l to form a blue-bright or clear passivate film.

The treating solution contains an oxidizing agent in an amount effective to activate the metal surface and to form a passivate film thereon, and iron and cobalt ions present in an amount effective to activate the bath and to impart integral initial hardness to the passivate film. The treating solution may optionally further contain cerium ions present in an amount effective to further activate the bath and to promote the formation of a clear light-yellow passivate film. Additionally, the treating solution may optionally contain halide ions including fluoride, chloride and bromide ions for increasing the hardness of the passivate film as well as one or more compatible wetting agents preferably in a small amount for achieving efficient contact with the substrate being treated.

The iron and cobalt ions are conveniently introduced into the bath by way of bath soluble and compatible salts including sulphates, nitrates, or halide salts. The concentration of the combined iron and cobalt ions to achieve appropriate activation of the treating bath is controlled within a range of about 0.02 to about 1 g/l, preferably within a range of about 0.1 to about 0.2 g/l. The iron and cobalt ions individually are present in an amount of about 0.01 to about 0.5 g/l with individual amounts of about 0.05 to about 0.1 g/l being preferred.

When a passivate film is desired having a light-yellow appearance, the treating bath further contains cerium ions present in an amount effective to further activate the bath and to impart a clear yellowish colour, preferably an iridescent light-yellow colour to the passivate film on the substrate treated. The cerium ions can be introduced in the form of any bath soluble and compatible cerium salt including cerium sulphate ($Ce(SO_4)_2 \cdot 4H_2O$); halide salts such as cerous chloride ($CeCl_3 \cdot 6H_2O$); or nitrate salts such as cerium nitrate ($Ce(NO_3) \cdot 5H_2O$), ($Ce(NO_3)_3(OH) \cdot 3H_2O$). Usually, at least some of the cerium ions are introduced into the bath in the tetravalent state to impart the characteristic yellow colour of the tetravalent cerium ion into the passivate film. Certain oxidizing agents such as hydrogen peroxide, act as a reducing agent under the acid conditions prevalent in the bulk of the operating bath and reduce some of the tetravalent cerium ions to the trivalent state. However, oxidizing agents such as hydrogen peroxide revert from a reducing agent to an oxidizing agent at the interface of the substrates being treated due to the higher pH prevalent at the interface and oxidize at least some of the trivalent cerium ions to the tetravalent state which are deposited in the film and impart the characteristic yellow colour thereto. When using such oxidizing agents as hydrogen peroxide, accordingly, all of the cerium ions can, if desired, be initially introduced into the operating bath in the trivalent state of which a portion are oxidized to the tetravalent state at the interface of the substrate. The passivate film usually contains a mixture of trivalent and tetravalent cerium compounds and the intensity of the yellow colour of the film is dictated by the concentration of the tetravalent cerium compounds present. The cerium ions in addition to imparting a light-yellow colour to the passivate film also improve the corrosion resistance of the treated substrate. The cerium sulphate compound, due to solubility difficulties, is preferably added to the bath in the form of an acid solution such as a dilute sulphuric acid solution containing the cerium sulphate dissolved therein.

The concentration of cerium ions in the operating bath can range from about 0.5 up to about 10 g/l with concentrations of from about 1.0 to about 4.0 g/l being preferred. The concentration of cerium ions is in part influenced by the magnitude of the yellow coating desired and higher concentrations of the cerium ions produce corresponding increases in the yellow colour of the passivate film.

Because of cost considerations, the cerium ions are preferably introduced as a commercially available mixtur of rare earth salts of metals in the lanthanide series which contains cerium compounds as the principal component. One such commercially available material is a cerous chloride solution containing about 46% solids of which $CeCl_3 \cdot 6H_2O$ predominates. The cerous chloride solution is derived from rare earth oxide (REO) concentrate sold by Molycorp, Inc. of White Plains, New Y rk under product code 5310 containing a minimum of 99 percent total REO of which CeO_2 is 96%, La_2O_3 is 2.7%, Nd_2O_3 is 1% and Pr_6O_{11} is 0.3%. A ceric sulphate solution is commercially available from the same source containing about 42% solids of which $Ce(SO_4)_2 \cdot H_2O$ predominates and which is also prepared from product code 5310 containing other rare earth metal compounds in similar minor amounts.

The operating bath in accordance with this first aspect of the present invention can conveniently be prepared by employing a concentrate containing the active constituents with the exception of the cerium ions and oxidizing agent which is adapted to be diluted with water to which the cerium ions, if employed, and oxidizing agent are separately added to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of the bath on a continuous or intermittent basis can be achieved employing a concentrate of the active constituents with the exception of the cerium ions and oxidizing agent which are individually added separately to the operating bath. Typically a bath make-up concentrate can contain from about 0.5 to about 50 g/l of iron and cobalt ions, halide ions up to about 20 g/l and a suitable surfactant in an amount up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 96 volume percent water to which cerium ions, if employed, and an oxidizing agent are added to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferably in a form commercially available containing from about 35 to 40 percent by volume hydrogen peroxide.

As previously advised, the low solubility of cerium sulphate makes it desirable to introduce this constituent into the operating bath in the form of an aqueous acidic solution. Normally, the use of cerium sulphate in the high concentrations necessary to form a concentrate with the remaining active constituents other than the peroxide constituent causes precipitation of the cerium compound. Even when the cerium is introduced as a halide or nitrate salt, the presence of sulphate ions in the concentrate employed introduced by the other constituents causes precipitation.

Accordingly, the cerium concentrate is preferably formed as a separate addition component and may comprise aqueous acidic solutions of cerous chloride or ceric sulphate having a cerium ion concentration of from about 200 to about 320 g/l and about 60 to 100 g/l, respectively. Such cerium concentrates may conveniently be comprised of the commercially available materials hereinbefore described available from Molycorp, Inc.

The treating bath contains hydrogen ions preferably in an amount to provide a pH of about 1.2 to about 2.5 with a pH range of about 1.5 to about 2.0 being preferred. Acidification of the operating bath to within the desired pH range can be achieved by a variety of mineral acids and organic acids such as sulphuric acid, nitric acid, hydrochloric acid, formic acid, acetic acid, or propionic acid of which sulphuric acid and nitric acid are preferred. The presence of sulphate ions in the bath has been found beneficial in achieving the desired passivation of the substrate and can be introduced by the sulphuric acid addition or sulphate salts of the other bath constituents. Sulphate ion concentrations can range in amounts up to about 15 g/l with concentrations of from about 0.5 to about 5 g/l being preferred.

The treating bath further contains an oxidizing agent or agents which are bath compatible of which peroxides including hydrogen peroxide and metal peroxides such as the alkali metal peroxides are preferred. Hydrogen peroxide itself of a commercial grade containing about 25% to about 60% by volume peroxide constitutes the preferred material. Other peroxides that can be employed include zinc peroxide. Additionally, ammonium and alkali metal persulphates have also been found effective as oxidizing agents.

The concentration of the oxidizing agent or mixture of oxidizing agents is controlled to achieve the desired surface appearance of the treated substrate. Typically, the concentration of the oxidizing agent can range from about 1 to about 20 g/l with an amount of about 3 to about 7 g/l being preferred, calculated on a weight equivalent effectiveness basis to hydrogen peroxide.

As an optional but preferred constituent, the bath may contain halide ions including chlorine, bromine and fluorine ions which have been found to enhance the hardness of the passivate film on the treated substrate. The halide ions or mixtures thereof can conveniently be introduced employing any of the alkali metal and ammonium salts thereof as well as salts of the metal ions hereinabove set forth. The concentration of the total halide constituent in the bath normally may range up to about 8 grams per litre with concentrations of about 0.1 to about 2.5 g/l being typical.

In the second fourth and fifth aspects of the invention it may be preferred that the concentration of the total halide constituent in the bath normally range up to about 2 grams per litre with concentrations of about 0.1 to about 0.5 g/l being typical.

In addition to the foregoing, the use of a small effective amount of a variety of bath compatible wetting agents also provides beneficial results in the nature of the passivate film deposited. When employed, the wetting agent can be present in concentrations up to about 1 g/l with concentrations of about 50 to about 100 mg/l being preferred.

Wetting agents suitable for use in the treating bath include aliphatic fluorocarbon sulphonates available from 3M und r the Fluorad brandname, such as, for example, Fluorad FC 98, which is a non-foaming wetting agent and its use at about 100 mg/l in the working bath improves the colour and hardness of the passivate film. A second class of suitable wetting agents is the sulpho-derivatives of succinates. An example of this class is Aerosol MA-80 which is dihexyl est r of sodium sulphosuccinic acid and is commercially available from American Cyanamid Company. A third class of suitable wetting agents is the sulphonates of naphthalene which are linear alkyl naphthalene sulphonates, such as Petro BA, for example, available from Petrochemical Company.

According to the second aspect of the pr sent invention there is provided a treating solution and

process which is effective to impart improved corrosion resistance to zinc, zinc alloy, cadmium and cadmium alloy, as well as aluminium and magnesium surfaces and to impart a desirable surfaces finish which can range from a clear bright to a light blue-bright appearance, which process is simpl to control and operate and which is of efficient and economical operation. This and the third to seventh aspects of the inventi n all utilize trivalent chromium ions.

The benefits and advantages of the second aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its essential constituents, chromium ions substantially all of which are present in the trivalent state preferably at a concentration of from about 0.05 grams per litre (g/l) up to saturation, hydrogen ions preferably to provide a solution pH of about 1.5 to about 2.2 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid or hydrochloric acid, an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, and iron ions preferably present in an amount of about 0.05 to about 0.5 g/l e.g in the ferric state in further combination with at least one additional metal ion selected from the group consisting of cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture and mixtures thereof present in an amount effective to impart increased corrosion resistance to the treated substrate and to activate the bath and the formation of a chromium passivate film on the substrate treated. As mentioned for the first aspect of the invention the solution may further optionally contain halide ions for imparting initial hardness to the coating, as well as a wetting agent.

In this second aspect of the invention whilst it is applicable in the same way as the first aspect, in the case of decorative zinc electroplatings, a further enhancement of the appearance of such substrates in addition to the corrosion resistance imparted is achieved by the passivate film which ranges from a clear bright to a light blue bright appearance simulating that of a chromium deposit.

The treating solution contains an oxidizing agent in an amount effective to activate the hydrated trivalent chromium to form a chromate film on the metal surface, iron ions present in the operating bath in the ferric state at a concentration ranging from about 0.05 to about 0.5 grams per litre and at least one additional metal ion selected from the group consisting of cobalt, nickel, molybdenum, manganese, lanthanum and mixtures thereof present in an amount effective to impart integral initial hardness to the gelatinous chromate film.

The trivalent chromium ions can be introduced in the form of any bath soluble and compatible salt such as chromium sulphate ($Cr_2(SO_4)_2$), chromium alum ($KCr(SO_4)_2$), chromium chloride ($CrCl_3$), chromium bromide ($CrBr_3$), chromium fluoride (CrF_3), or chromium nitrate ($CrNO_3$). The trivalent chromium ions can also be introduced by a reduction of a solution containing hexavalent chromium ions employing an appropriate reducing agent of any of the types well known in the art to effect a substantially complete stoichiometric reduction of all of the hexavalent chromium to the trivalent state.

what is saturation ?

The concentration of the trivalent chromium ions in the treating solution may range from as low as about 0.05 g/l up to saturation with quantities of about 0.2 to 2 g/l being preferred. Typically, the operating bath contains from about 0.5 to about 1 g/l trivalent chromium ions.

The treating solution further contains iron ions preferably present in an amount of about 0.05 to about 0.5 g/l with concentrations ranging from about 0.1 to about 0.2 g/l being preferred. The iron ions in the operating bath are predominantly in the ferric state due to the presence of bath oxidizing agents although they can be added in the ferrous form. As in the case of the chromium ions, the iron ions can be added to the bath in the form of any bath soluble and compatible iron salt such as ferrous ammonium sulphate, ferric sulphate, ferric nitrate, or iron halide salts. Of the foregoing, ferric sulphate comprises the preferred material for economic reasons and because the use of this salt also introduces the desired sulphate ions into the solution.

In addition to the iron ions, the bath further contains at least one additional metal ion selected from the group consisting of cobalt, nickel, molybdenum, manganese, lanthanum, as well as mixtures thereof. The foregoing metal ions or mixtures of metal ions are conveniently introduced as in the case of the iron ions, by way of bath soluble and compatible metal salts including the sulphates, nitrates or halide salts. For economic reasons, the lanthanum ions are preferably introduced not as a pure lanthanum compound, but as a mixture of the rare earth salts of the metals of the lanthanide series. (hereinafter designated as "lanthanide mixture") which contains lanthanum compounds as the predominant constituent. A commercially available lanthanide mixture which is suitable for use in the practice of the present invention is Lanthanum-Rare Earth Chloride, product code 5240, available from Molycorp, Inc. of White Plains, New York. This product has the general formula LA —$RECl_3 \cdot 6H_2O$ and is available as a solution containing about 55 to 60% by w ight solids. The solution is prepared from a rare earth oxide (REO) concentrate containing a minimum of 46% by weight total REO comprising about 60% lanthanum oxide (La_2O_3), 21.5% n odymium oxide (Nd_2O_3), 10% cerium oxid (CeO_2), 7.5% praseodymium oxide (Pr_6O_{11}) and 1% of residual REO.

The presence of such other rare arth metals in the solution do s not appear to have any adverse effect at the low concentrations in which they are present and may further contribut to the activation of the treating solution in forming the passivate film.

The concentration of the additi nal metal ions for appropriate activation of th tr ating bath is

controlled t provide a concentration ranging from about 0.02 up to about 1 g/l with concentrations of from about 0.1 to about 0.2 g/l being preferred.

The operating bath in accordance with this second aspect of the invention can conveniently b prepared by employing a concentrate containing the active constituents with the exception of the oxidizing agent which is adapted to be diluted with water to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of the bath on a continuous or intermittent basis can be achieved employing a concentrate of the active constituents with the exception of the oxidizing agent which is added separately to the operating bath. Typically, a bath make-up concentrate can contain from about 10 to about 30 g/l chromium ions, about 0.5 to about 10 g/l iron ions, from about 5 to about 50 g/l of at least one additional metal ion of the group consisting of cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture or mixtures thereof, halide ions up to about 20 g/l and a suitable surfactant in an amount up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 98.5 volume percent water to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferably in a form commercially available ~~containing~~ from about 35 to 40 percent by volume hydrogen peroxide.

According to the third aspect of the present invention there is provided a treating solution and process which is ~~effective to impart~~ a clear light-yellow passivate film to zinc, zinc alloy, cadmium, cadmium alloy, aluminium and magnesium surfaces which provides for improved corrosion resistance approaching or comparable to that heretofore obtained employing conventional hexavalent chromium passivating solutions. The present invention is further characterized by a process which is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the third aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its essential constituents, chromium ions substantially all of which are present in the trivalent state preferable at a concentration of from about 0.05 grams per litre (g/l) up to saturation, hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid, or hydrochloric acid; an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, and cerium ions present in an amount effective to activate the bath and the formation of a clear light-yellow chromium passivate film on the treated substrate.

In addition to the cerium ions in the treating solution, the solution may optionally and preferably further contain an additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixtures as well as mixtures thereof to provide a further activation of the bath and passivate film formation. As mentioned for the earlier aspects of the invention the solution may optionally also contain halide ions for imparting hardness to the coating in addition to a small amount of a wetting agent. The cerium ions can be introduced with the treating solution in this third aspect of the invention in the same manner as described for the first aspect of the invention.

In addition to the cerium ions, the bath may further optionally and preferably contain at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixtures as well as mixtures thereof. Such metal ions may be introduced into the treating solution in this third aspect of the invention in the same manner as already described for the second aspect.

The operating bath in accordance with this third aspect of the invention can conveniently be prepared by employing a concentrate containing the active constituents with the exception of the cerium ions and oxidizing agent which is adapted to be diluted with water to which the cerium ions and oxidizing agent are separately added to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of the bath on a continuous or intermittent basis can be achieved employing a concentrate of the active constituents with the exception of the cerium ions and oxidizing agent which are individually added separately to the operating bath. Typically a bath makeup concentrate can contain from about 10 to about 80 g/l chromium ions, from about 0.5 to about 50 g/l of additional metal ions of the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture, or mixtures thereof, halide ions up to about 20 g/l and a suitable surfactant in an amount up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 96 volume percent water to which cerium ions and an oxidizing agent are added to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferable in a form commercially available containing from about 35 to 40 percent by volume hydrogen peroxide.

As previously advised, the low solubility of cerium sulphate makes it desirable to introduce this constituent into the op rating bath in the form of an aqueous acidic solution. Normally, the use of cerium sulphate in the high concentrations necessary to form a concentrate with the remaining active constituents other than the peroxide constituent causes precipitation of the cerium compound. Even when the cerium is introduced as a halide or nitrate salt, the presenc of sulphate ions in the concentrate employed introduced by the other constituents causes precipitation. Accordingly, the

cerium concentrate is preferably formed as a separate addition component and may comprise aqueous acidic solutions of cerous chloride or ceric sulphate having a cerium ion concentration of from about 200 to about 320 g/l and about 60 to 100 g/l, respectively. Such cerium concentrates may conveniently be comprised of the commercially availabl materials hereinbefore described available from Molycorp, Inc.

According to the fourth aspect of the present invention there is provided a treating solution and process which is effective to impart improved corrosion resistance to zinc, zinc alloy, cadmium and cadmium alloy, as well as aluminium and magnesium surfaces and to impart a desirable surface finish which can range from a clear bright to a light blue-bright to a yellow iridescent appearance, which produces a passive film of improved clarity and initial hardness, which process is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the fourth aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its essential constituents, chromium ions substantially all of which are present in the trivalent state preferably at a concentration of from about 0.05 grams per litre (g/l) up to saturation, (and which can be introduced as discussed for the second and third aspects), hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid, or hydrochloric acid, an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, a bath soluble and compatible organic carboxylic acid present in an amount effective to impart initial hardnes and clarity to the passive film, the said organic acid having the structural formula:

$$(OH)_a\,R\,(COOH)_b$$

Wherein:

a is an integer from 0 to 6;

b is an integer from 1 to 3; and

R represents an alkyl, alkenyl, or aryl group containing from C_1 to C_6 carbon atoms;

as well as the bath soluble and compatible salts thereof, and at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, cerium and lanthanide mixtures, as well as mixtures thereof present in an amount effective to activate the bath and formation of a chromium passivate film of the desired appearance on the substrate treated desirably imparting initial hardness to the gelatinous chromate film. As mentioned for the earlier aspects of the invention the solution may further optionally contain halide ions for imparting additional hardness to the coating, as well as a wetting agent. In this fourth aspect of the invention whilst it is applicable in the same way as the first aspect in the case of decorative zinc electroplatings, a further enhancement of the appearance of such substrates in addition to the corrosion resistance imparted is achieved by the passivate film which ranges from a clear bright to a light blue bright appearance simulating that of a chromium deposit or alternatively, a clear light-yellow appearance simulating that obtained by use of a prior art hexavalent chromium solutions.

In addition, the bath further contains at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixtures and cerium, as well as mixtures thereof. The foregoing metal ions or mixtures of metal ions are conveniently introduced into the bath by way of bath soluble and compatible metal salts including the sulphates, nitrates or halide salts, as discussed for the second and third embodiments and such materials as are discussed above for those aspects can be and desirably are used in this aspect of the invention.

The concentration of the additional metal ions other than cerium ions for appropriate activation of the treating bath to produce a clear to blue-bright appearance is controlled to provide a concentration ranging from about 0.02 up to about 1 g/l with concentrations of from about 0.1 to about 0.2 g/l being preferred. While such metal ions can be used in concentrations above 1 g/l, such as, up to 10 g/l, the use of such higher concentrations even in the absence of cerium ions tends to produce dull films of a yellow tint rather than the desired clear or light-blue films. For this reason, such higher concentrations are undesirable from an appearance standpoint.

A further essential constituent of the improved bath of the present invention comprises an organic carboxylic acid or salt thereof of the structural formula as hereinbefore set forth present in an amount effective to impart increased clarity and initial hardness to the gelatinous chromate film deposited. The unexpected improvement in clarity of the film is particularly pronounced in connection with the light-yellow iridescent films produced from cerium ion containing solutions. The particular concentration or range of concentrations of the clarity/hardness agent will vary in proportion to molecular weight of the particular acid and/or metal salt employed with higher concentrations required for an equivalent effectiveness as the molecular weight of the additive agent increases. The particular concentration to achiev optimum clarification and hardness is also dictated to some extent by the concentration of th other metal ions present in the bath with higher concentrations being used as the metal i n concentrations increase. Generally, the organic carboxylic acid additive agent or metal salts thereof can be employed in amounts ranging from about 0.05 up to about 4.0 g/l with concentrations of about 0.1 to about 1.0 g/l being usually preferred.

The additive can be introduced as the organic acid itself or as any bath soluble and compatible metal salt including the alkali metal salts, ammonium salts and salts of the several additional metal ions in the bath. For economic reasons, the organic acid is usually introduced as an acid or as the sodium or potassium salt thereof.

Within the scope of the structural formula as hereinabove set forth, organic carboxylic acids which have been found particularly suitable include malonic, maleic, succinic, gluconic, tartaric and citric acids, of which succinic and or succinate salts have been found particularly effective.

The operating bath in accordance with this fourth aspect of the invention can conveniently be prepared by employing a concentrate containing the active ingredients with the exception of the oxidizing agent and cerium ions, if used, which is adapted to be diluted with water to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of the bath on a continuous or intermittant basis can be achieved employing a concentrate of the active constituents with the exception of the oxidizing agent and cerium ions, if used, which is added separately to the operating bath. Typically, a bath make-up concentrate can contain from about 10 to about 80 g/l chromium ions, from about 1.0 to about 80 g/l of the organic carboxylic acid and/or salt additive agent, from about 5 to about 50 g/l of at least one additional metal ion of the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture or mixtures thereof, halide ions up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 98 volume percent water to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferably in a form commercially available containing from about 35 to 40 percent by volume hydrogen peroxide. The cerium ions when employed, are preferably introduced in the form of an aqueous acid solution of cerous chloride or ceric sulphate having cerium ion concentration of from about 200 to about 320 g/l and about 60 to about 100 g/l, respectively. Such cerium concentrates may be conveniently comprised of the commercially available materials hereinbefore described available from Molycorp, Inc.

According to the fifth aspect of the present invention there is provided a treating solution which aims to reduce the severity of a problem of loss of oxidizing agent associated with prior art baths. Thus while improvements have been made in trivalent chromium passivate compositions and processes to produce commercially acceptable passivate films, a continuing problem associated with such operating baths has been the relatively rapid loss of the peroxide-type oxidizing agent, particularly hydrogen peroxide, which is present as a necessary bath constituent to achieve acceptable passivate films. Such prior art operating baths also undergo a relatively rapid rise in pH necessitating careful control and addition of acids to maintain the pH level within the optimum operating range. The progressive loss of the peroxide-type oxidizing agent, particularly hydrogen peroxide, is due in part to the presence of activating metal ions present in the solution as well as contaminating metal ions such as zinc or cadmium, for example, introduced by dissolution of the metal from the substrates being treated which tend to catalyze a decomposition of the peroxide oxidizing agent. The progressive loss of the peroxide-type oxidizing agents occurs not only during processing but also during standing of the bath overnight and over weekends during plant shutdown. Typically, a fresh operating bath containing 3% by volume of a 35% solution of hydrogen peroxide on standing overnight will lose about 0.1% by volume per hour of the hydrogen peroxide oxidizing agent while a used solution containing from about 2 to about 10 grams per litre of contaminating zinc ions will experience a loss of hydrogen peroxide at a rate as great as about 0.4% by volume per hour. It will be apparent from the foregoing that careful monitoring of the operating bath composition and frequent replenishment of the peroxide oxidizing agent is required to maintain opti~~mum bath~~ efficiency which is not only costly but also time consuming.

Thus this fifth aspect of the present invention aims to provide a treating solution and process which is effective ~~to impart im~~proved corrosion resistance to zinc, zinc alloy, cadmium and cadmium alloy, as well as aluminium and magnesium surfaces and to impart a desirable surface finish which can range from a clear bright to a light blue-bright to a yellow iridescent appearance, which produces a passivate film of improved corrosion resistance, hardness, durability, clarity and initial hardness, which provides a treating solution that is stabilized against rapid loss of the peroxide oxidizing agent and against a rapid rise in pH, which process is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the fifth aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its ssential constituents, chromium ions substantially all of which are present in the trivalent stat preferably at a concentration of from about 0.05 grams per litre (g/l) up to saturation (and which can be introduced as discussed for the second to fourth aspects), hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid, hydrochloric acid or the like, an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, a stabilizing additive comprising a mixture of 1-hydroxyethylidene-1,1 diphosphonic acid and citric acid and the bath compatibl and soluble salts thereof present in an amount effective to reduce loss of the peroxide oxidizing agent and to stabilize the pH of the operating bath, and at least one additional metal

i n selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures, and cerium as well as mixtures thereof present in an amount effective to activate the bath and formation of a chromium passivate film of the desired appearance on the substrate treated. As mentioned for the earlier aspects of the invention th solution may optionally contain halide ions for imparting additional hardness t the coating, and optionally, a wetting agent. It may also incorporate a bath soluble and compatible silicate compound present in an amount effective to impart increased corrosion resistance and hardness to the passivate film e.g. in an amount of about 0.01 to about 5 g/l calculated as SiO_2 as discussed in connection with the sixth aspect below. It may also incorporate a bath soluble compatible organic carboxylic acid present in an amount effective to further impart initial hardness and clarity to the passivate film as discussed in connection with the fourth aspect above.

In this fifth aspect of the invention whilst it is applicable in the same way as the first aspect in the case of decorative zinc electroplatings, a further enhancement of the appearance of such substrates in addition to the corrosion resistance imparted is achieved by the passivate film which ranges from a clear bright to a light blue bright appearance simulating that of a chromium deposit or alternatively, a clear light-yellow appearance simulating that obtained by use of prior art hexavalent chromium solutions.

A further essential constituent of the treating bath in accordance with the fifth aspect of the invention is the stabilizing agent comprising a mixture of 1-hydroxy ethylidene-1,1 diphosphonic acid and citric acid as well as the bath soluble and compatible salts thereof. The combination of the diphosphonic and citric acid constituents appears to provide a synergistic action in not only reducing the decomposition and rate of loss of the peroxide-type oxidizing agent but also in stabilizing the pH of the operating bath preventing a rapid rise as had heretofore been experienced in prior art-type trivalent chromium passivation treating solutions. Typically, the two stabilizing constituents are added in the acid form or as the alkali metal or ammonium salts thereof. A commercially available material suitable for use is sold under the brand name Dequest 2010 by Monsanto Chemical Company and comprises 1-hydroxy ethylidene-1,1 diphosphonate.

The diphosphonic acid or diphosphonate constituent can be present in the operating bath in an amount of about 0.05 up to about 3 g/l with amounts of about 0.1 to about 0.5 g/l being preferred. The citric acid or citrate constituent can be present in the operating bath from about 0.1 to about 10 g/l with amounts of about 0.5 to about 1.5 g/l being preferred.

An optional but preferred constituent of the treating bath comprises a silicate compound present in an amount effective to provide an improved corrosion protection and hardness to the passivate film formed on the treated substrates. The silicates to be used and the amounts in which they should be used are discussed in more detail below in connection with the sixth aspect of the present invention.

In addition, the bath further contains at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures and cerium as well as mixtures thereof. The foregoing metal ions or mixtures of metal ions are conveniently introduced into the bath by way of bath soluble and compatible metal salts including the sulphates, nitrates, or halide salts, as discussed for the second to fourth aspects and such materials as are discussed above for those aspects can be and desirably are used in this aspect of the invention.

The foregoing metal ions or combinations thereof with the exception of cerium ions are employed for producing a clear to a light-blue passivate film. When a light-yellow iridescent passivate film is desired, cerium ions are employed, preferably in combination with one or more of the other metal ions to produce a passivate film simulating in appearance the light yellow passivate films heretofore obtained employing hexavalent chromium passivating solutions which have been recognised and embodied is ASTM specifications in view of their characteristic colour and associated excellent corrosion resistance. The cerium ions can be introduced in the manner discussed above in connection with the first third and fourth aspects.

The concentration of the additional metal ions other than cerium ions for appropriate activation of the treating bath to produce a clear to blue-bright appearance should be controlled in the manner discussed in connection with the fourth aspect of the invention.

When the operating bath is to contain an organic carboxylic acid or salt thereof as discussed in connection with the fourth aspect of the present invention, the teaching there given should be followed. However, the presence of a silicate compound in the operating bath as discussed below in connection with the sixth aspect of the present invention has been found to also contribute to improved clarity of the passivate film, and accordingly, the use of the organic carboxylic acid addition agent is usually unnecessary when a silicate compound is employed in the bath.

The operating bath in accordance with this fifth aspect of the invention can conveniently be prepared by employing a concentrate containing the active constituents with the exception of the oxidizing agent and cerium ions, if used, which is adapted to be diluted with water to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of th bath on a continuous or intermittent basis can be achieved employing a concentrate of the active constituents with the exception of the oxidizing agent and cerium ions, if used, which is added separately to the operating bath. Typically, a bath make-up concentrate can contain from about 10

about 80 g/l chromium ions, from about 5 to about 50 g/l of at least one additional metal ion of the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture or mixtures thereof, halide ions up to about 50 g/l, from about 5 to about 30 g/l of a silicate compound, if used, calculated as SiO_2; and a suitable surfactant in an amount up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 98 volume percent water to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferably in a form commercially available containing from about 35 to 40 percent by volume hydrogen peroxide. The cerium ions, when employed, are preferably introduced in the form of an aqueous acid solution of cerous chloride or ceric sulphate having cerium ion concentration of from about 200 to about 320 g/l and about 60 to about 100 g/l, respectively. Such cerium concentrates may be conveniently comprised of the commercially available materials hereinbefore described available from Molycorp, Inc.

The foregoing trivalent chromium concentrate containing the metal ions and acid components in combination with an inorganic silicate compound has a tendency to form precipitates during prolonged storage due to the high concentration and acidic conditions present. Accordingly, such foregoing concentrates are normally diluted with water shortly after preparation to provide an operating bath containing the active constituents in the desired concentrations. Concentrates of substantially improved stability and prolonged shelf storage life can be provided by the use of organic silicates as discussed below in connection with the sixth aspect in combination with the trivalent chromium ions, and optionally, halide ions and a wetting agent. Such stable concentrations conventionally contain from about 10 to about 80 g/l trivalent chromium ions, about 5 up to about 50 g/l of an organic quaternary ammonium silicate calculated as SiO_2, halide ions up to about 50 g/l and a surfactant in an amount up to about 5 g/l. Such stable concentrate is adapted to be used in conjunction with a second concentrate containing the acid components, the additional metal ions in an amount of about 5 to about 50 g/l, up to 80 g/l of the organic carboxylic acid and/or salt additive agent if used. Such second concentrate can also optionally contain a portion or all of the halides and wetting agents if not employed in the first trivalent chromium concentrate.

In the preparation of such a trivalent chromium/silicate concentrate, the organic silicate is first diluted with water to the desired concentration range whereafter the trivalent chromium constituent is added along with the optional halide and wetting agent, if employed. A particularly suitable commercially available organic silicate compound comprises Quram 220 available from Emery Industries which comprises a quaternary amine silicate.

The diphosphonic acid and citric acid and/or diphosphonate and citrate stabilizing additive can be incorporated in any of the foregoing concentrates including the peroxide concentrate in an amount to attain the desired concentration in the operating bath. Alternatively, the stabilizing additive can be prepared as a separate aqueous concentrate containing from about 30 to about 170 g/l of the diphosphonic/diphosphonate compound in admixture with about 160 to about 500 g/l of the citric acid/citrate compound and added separately to the operating bath to provide the desired working concentration in accordance with the limits hereinbefore specified, and typically, 4—5 g/l of the stabilizer concentrate. In accordance with a preferred practice, the stabilizing additive is incorporated directly in the chromium containing concentrate, the cerium ion concentrate in the case of a yellow passivate process, or in the second concentrate employed in conjunction with the organic silicate concentrate in amounts of about 3 to about 17 g/l diphosphonic acid/diphosphonate compound and about 16 to about 50 g/l citric acid/citrate compound.

As discussed above for the first to fourth aspects the treating bath can be applied to the substrate in a variety of ways and the process conditions described for these aspects can and desirably should be used for this fifth aspect of the present invention.

At the conclusion of the passivation treatment, the substrate is extracted from the treating solution and is dried such as by warm circulating air. Ordinarily, such passivated substrates, particularly work pieces processed while supported on a work rack are characterised as having a uniform passivate film over the surfaces thereof requiring no further processing. In the case of small work pieces which are treated in bulk such as in a rotating processing barrel, some damage such as scratches can occur in the passivate film during treatment and it is desirable in such instances to subject such work pieces to a post silicate rinse treatment (as discussed below as the seventh aspect of the present invention) to s al any such surfac imperfections thereby substantially improving the corrosion protection of barrel-processed parts.

When such an optional post passivation silicate rinse treatment is employed, the substrate following the passivation treatment is preferably subjected to at least one or a plurality of water rinse steps usually at room temperature to remove residual passivate solution from the surfaces thereof whereafter the substrates are contacted with the post silicate rinse solution in accordance with the teaching given below in connection with the seventh aspect of the present invention.

According to the sixth aspect of the present invention there is provided a treating solution which aims to reduce the severity of a problem of damage to the passivate of passivated workpiec s during subsequent processing. Thus while improvements hav been made in trivalent chromium passivate

compositions and processes to produce commercially acceptable passivate films, such films as initially formed have been found in some instances to lack sufficient initial hardness to enable handling of the substrate through further work stages without encountering damage to the passivate film. Additionally, such trivalent chromium passivate compositions and processes have also been found in some instances to lack optimum corrosion resistance, hardness and durability and produce films which are somewhat cloudy and lack optimum clarity from an appearance standpoint.

Thus this sixth aspect of the present invention aims to provide a treating solution and process which is effective to impart improved corrosion resistance to zinc, zinc alloy, cadmium and cadmium alloy, as well as aluminium and magnesium surfaces and to impart a desirable surface finish which can range from a clear bright to a light blue-bright to a yellow iridescent appearance, which produces a passivate film of improved corrosion resistance, hardness, durability, clarity and initial hardness, which process is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the sixth aspect of the present invention are achieved in accordance with the composition aspects thereof by providing an aqueous acidic treating solution containing as its essential constituents, chromium ions substantially all of which are present in the trivalent state preferably at a concentration of from about 0.05 grams per litre (g/l) up to saturation (and which can be introduced as discussed for the second to fifth aspects), hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid, or hydrochloric acid, an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, a bath soluble and compatible silicate compound present in an amount effective to impart increased corrosion resistance and hardness to the passivate film (preferably present in an amount of about 0.01 to about 5 g/l calculated as SiO_2), and at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures and cerium, as well as mixtures thereof present in an amount effective to activate the bath and formation of a chromium passivate film of the desired appearance on the substrate treated. As mentioned for the earlier aspects of the invention, the solution may optionally contain halide ions for imparting additional hardness to the coating, and optionally a wetting agent. It may also incorporate a bath soluble compatible organic carboxylic acid present in an amount effective to further impart initial hardness and clarity to the passivate film.

In this sixth aspect of the invention whilst it is applicable in the same way as the first aspect in the case of decorative zinc electroplatings, a further enhancement of the appearance of such substrates in addition to the corrosion resistance imparted is achieved by the passivate film which ranges from a clear bright to a light blue bright appearance simulating that of a chromium deposit or alternatively, a clear light-yellow appearance simulating that obtained by use of prior art hexavalent chromium solutions.

A further essential constituent of the treating bath in accordance with the sixth aspect of the invention is the silicate compound present in an amount effective to provide an improved corrosion protection and hardness to the passivate film formed on the treated substrate. The silicate compound may comprise a bath soluble and compatible inorganic or organic silicate compound as well as mixtures thereof which are preferably present in an amount of about 0.01 up to about 5 g/l calculated as SiO_2 with concentrations of about 0.1 to about 0.5 g/l being preferred. When inorganic silicates are employed, concentrations above about 2 g/l in the operating bath are undesirable because of the tendency of the silicate to form fine flocculent precipitates with the metal ions present in the bath under the acidic conditions present which contributes towards bath instability. Organic silicates, on the other hand, provide for improved bath stability and are preferred for the formation of make-up and replenishment concentrates because of the improved stability and prolonged shelf life.

Inorganic silicates suitable for use in the practice of the present invention include alkali metal and ammonium silicates of which sodium silicate ($Na_2O \cdot xSiO_2$ (x=2—4) and potassium silicate ($K_2O \cdot ySiO_2$ (y=3—5) are preferred for economic reasons. Organic silicates which can also be satisfactorily employed include quaternary ammonium silicates which include tetramethyl-ammonium silicate, phenyltrimethylammonium silicate, disilicate and trisilicate, and benzyltrimethylammonium silicate and disilicate. Such silicates meeting the purposes of this invention may be expressed by the following general formula:

$$ROR' {:} xSiO_2 {:} yH_2O$$

Where R represents a quaternary ammonium radical substituted with four organic groups selected from the groups alkyl, alkylene, alkanol, aryl, arkylaryl or mixtures thereof, R' represents either R or a hydrogen atom, x equals 1 to 3 and y equals 0 to 15.

Such water soluble organic silicates including their synthesis and characterization are more fully described in th literatur such as the article by M rrill and Spencer, "Some Quaternary Ammonium Silicates", published in the Journal of Physical and Colloid Chemistry, 55, 187 (1951), the substance of which is incorporated herein by reference. Similar silicates including typical synthesis thereof are disclosed in United States Patent 3,993,548 to which reference is also made for further details.

In addition, the bath further contains at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures and cerium as well as mixtures thereof. The foregoing metal ions or mixtures of metal ions are conveniently introduced into the bath by way of bath soluble and compatible metal salts including the sulphates, nitrates, halide salts, as discussed for the second to fifth aspects and such materials as are discussed above for those aspects can be and desirably are used in this aspect of the invention.

The foregoing metal ions or combinations thereof with the exception of cerium ions are employed for producing a clear to a light-blue passivate film. When a light-yellow iridescent passivate film is desired, cerium ions are employed, preferably in combination with one or more of the other metal ions to produce a passivate film simulating in appearance the light yellow passivate films heretofore obtained employing hexavalent chromium passivating solutions which have been recognized and embodied in ASTM specifications in view of their characteristic colour and associated excellent corrosion resistance. The cerium ions can be introduced in the manner described above in connection with the first, third, fourth and fifth aspects.

The concentration of the additional metal ions other than cerium ions for appropriate activation of the treating bath to produce a clear to blue-bright appearance should be controlled in the manner discussed in connection with the fourth and fifth aspects of the present invention.

When the operating bath is to contain an organic carboxylic acid or salt thereof as discussed in the fourth and fifth aspects of the present invention the teaching there given should be followed.

The presence of the silicate compound in the operating bath in accordance with this sixth aspect of the invention has unexpectedly been found to also contribute to improved clarity of the passivate film, and accordingly, the use of the organic carboxylic acid addition agent is not essential when a silicate is present in the bath in accordance with this aspect of the invention though it may be desirable.

The operating bath in accordance with this sixth aspect of the invention can conveniently be prepared by employing a concentrate containing the active constituents with the exception of the oxidizing agent and cerium ions, if used, which is adapted to be diluted with water to form a bath containing the constituents within the desired concentration range. Similarly, replenishment of the bath on a continuous or intermittent basis can be achieved employing a concentrate of the active constituents with the exception of the oxidizing agent and cerium ions, if used, which is added separately to the operating bath. Typically, a bath make-up concentrate can contain from about 10 to about 80 g/l chromium ions, from about 5 to about 30 g/l of the silicate compound calculated as SiO_2, from about 5 to about 50 g/l of at least one additional metal ion of the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture or mixtures thereof, halide ions up to about 50 g/l and a suitable surfactant in an amount up to about 5 g/l if employed. Such a make-up concentrate is adapted to be diluted with about 98 volume percent water to produce an operating bath containing the active constituents within the ranges specified. The oxidizing agent such as hydrogen peroxide, for example, is separately introduced into the bath preferably in a form commercially available containing from about 35 to 40 percent by volume hydrogen peroxide.

The cerium ions, when employed, are preferably introduced in the form of an aqueous acid solution of cerous chloride or ceric sulphate having cerium ion concentration of from about 200 to about 320 g/l and about 60 to about 100 g/l, respectively. Such cerium concentrates may be conveniently comprised of the commercially available materials hereinbefore described available from Molycorp, Inc.

The foregoing trivalent chromium concentrate containing the silicate compound, metal ions and acid components has a tendency to form precipitates during prolonged storage due to the high concentrations and acidic conditions present. Accordingly, such foregoing concentrates are normally diluted with water shortly after preparation to provide an operating bath containing the active constituents in the desired concentrations. It has been further discovered in accordance with this sixth aspect of the present invention that concentrates of substantially improved stability and prolonged shelf storage life can be provided by the use of organic silicates of the types heretofore set forth in combination with the trivalent chromium ions and, optionally, halide ions and a wetting agent. Such stable concentrates conveniently contain from about 10 to about 80 g/l trivalent chromium ions, about 5 up to about 50 g/l of an organic quaternary ammonium silicate calculated as SiO_2, halide ions up to about 50 g/l and a surfactant in an amount up to about 5 g/l. Such stable concentrate is adapted to be used in conjunction with a second c ncentrate containing the acid components, the additional metal ions in an amount of about 5 to about 100 g/l, up to 80 g/l of the organic carboxylic acid and/or salt additive agent if used. Such second concentrate can also optionally contain a portion or all of the halid s and w tting agents if not employed in the first trivalent chromium concentrate.

In the preparation of such a trivalent chromium/silicate concentrate, the organic silicat is first diluted with water to the desired concentration range whereafter the trivalent chromium constituent is added along with the optional halide and wetting agent if employed. A particularly suitable commercially available organic silicate compound comprises Quram 220 available from Emery Industries which comprises a quaternary amine silicat .

This sixth aspect of the present invention further encompasses a novel concentrate composition

suitable for make-up of the operating bath by dilution with water containing as its essential constituents trivalent chromium ions and an organic quaternary ammonium silicate which provides compatibility and storage stability over prolonged time periods.

As discussed above for the first to fifth aspects the treating bath can be applied to the substrate in a variety of ways and the process conditions described for these aspects can and desirably should be used for this sixth aspect of the present invention.

At the conclusion of the passivation treatment, the substrate is extracted from the treating solution and is dried such as by warm circulating air. Ordinarily, such passivated substrates, particularly work pieces processed while supported on a work rack are characterized as having a uniform passivate film over the surfaces thereof requiring no further processing. In the case of small work pieces which are treated in bulk such as in a rotating processing barrel, some damage such as scratches can occur in the passivate film during treatment and is desirable in such instances to subject such work pieces to post silicate rinse treatment (as discussed below as the seventh aspect of the present invention) to seal any such surface imperfections thereby substantially improving the corrosion protection of the barrel-processed parts.

When such an optional post passivation silicate rinse treatment is employed, the substrate following the passivation treatment is preferably subjected to at least one or a plurality of water rinse steps usually at room temperature to remove residual passivate solution from the surfaces thereof whereafter the substrates are contacted with the post silicate rinse solution in accordance with the teaching given below in connection with the seventh aspect of the present invention.

According to the seventh aspect of the present invention there is proved a treating process which addresses the same problem as the sixth aspect of the present invention namely that of damage to the passivate of the passivated work pieces during subsequent processing. Thus while improvements have been made in trivalent chromium passivate compositions and processes to produce commercially acceptable passivate films, such films as initially formed have been found in some instances to lack sufficient initial hardness to enable handling of the substrate through further work stages without encountering damage to the passivate film. Additionally, such trivalent chromium passivate compositions and processes have also been found in some instances to lack optimum corrosion resistance, hardness and durability, and produce films which are somewhat cloudy and lack optimum clarity from an appearance standpoint.

Thus the seventh aspect of the present invention aims to provide a process which is effective to impart improved corrosion resistance to zinc, zinc alloy, cadmium and cadmium alloy, as well as aluminium and magnesium surfaces and to impart a desirable surface finish which can range from a clear bright to a light blue-bright to a yellow iridescent appearance, which produces a passivate film of improved corrosion resistance, hardness, durability, clarity and initial hardness, which process is simple to control and operate and which is of efficient and economical operation.

The benefits and advantages of the seventh aspect of the present invention are achieved by a process which provides an aqueous acidic treating solution containing as its essential constituents,

Cr^{3+}

chromium ions substantially all of which are present in the trivalent state preferably at a concentration of from about 0.05 grams per litre (g/l) up to saturation, (and which can be introduced as discussed for the second to sixth aspects) hydrogen ions preferably to provide a solution pH of about 1.2 to about 2.5 which can be conveniently introduced by mineral acids such as sulphuric acid, nitric acid, or hydrochloric acid, an oxidizing agent of which hydrogen peroxide itself is preferred, preferably present in an amount of about 1 to about 20 g/l, at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures and cerium as well as mixtures thereof, contacting the substrate with the said aqueous acidic solution for a period of time sufficient to form a passivate film thereon, and contacting for a period of at least about one second the passivated substrate with a dilute aqueous rinse solution containing a bath soluble and compatible silicate compound present in an amount effective to impart improved corrosion resistance and hardness to the passivate film, and thereafter drying the passivated silicate rinsed substrate.

The aqueous acidic solution may be as described in connection with any of the first to sixth foregoing aspects, and it may be used in the same way.

Following the passivation treatment, the substrate is preferably subjected to one or a plurality of water rinse steps which may be at room temperature or at elevated temperatures whereafter the passivated substrate is contacted with a dilute aqueous silicate solution in the form of a final rinse step. The contact time of the passivated substrate with the silicate solution may range for a period of at least about one s cond up to about one minute or longer and the silicate solution may range in temperature from about 50° up to about 150°F (10° to 66°C). Following the silicate rinse step, the substrate is dried such as by circulating hot air, for example.

The aqueous silicate rinse solution preferably contains as its essential constituent, a bath soluble and compatible inorganic or organic silicate compound as well as mixtures thereof present in an amount of about 1 to about 40 g/l, and preferably from about 5 to about 15 g/l (calculated as SiO_2). In organic silicates suitable for use in the practice of the present process include alkali metal and ammonium silicates of which sodium silicate ($Na_2O \cdot xSiO_2$ (where x equals 2 t 4)) and potassium

silicate ($K_2O \cdot ySiO_2$ (where y equals 3 to 5)) are preferred for economic reasons. Organic silicates which can also be satisfactorily employed include quaternary ammonium silicates which include tetramethylammonium silicate, phenyltrimethylammonium silicate, disilicate and trisilicate, and benzyltrimethylammonium silicate and disilicate. Such silicates suitable for use in the present invention have the following general formula:

$$ROR' {:} xSiO_2 {:} yH_2O$$

Where R represents a quaternary ammonium radical substituted with four organic groups selected from the groups alkyl, alkylene, alkanol, aryl, alkylaryl or mixtures thereof, and R' represents either R or a hydrogen atom, and x equals 1 to 3 and y equals 0 to 15.

Such water soluble organic silicates and their synthesis and characterization are more fully described in the literature such as the article by Merrill and Spencer, "Some Quaternary Ammonium Silicates", published in the Journal of Physical and Colloid Chemistry, 55, 187 (1951), the substance of which is incorporated herein by reference. Similar silicates and a typical synthesis thereof are disclosed in United States Patent 3,993,548 to which reference is also made for further details.

Because of the relatively higher cost of such organic silicates, the silicate rinse solution preferably comprises inorganic silicates of which the potassium and sodium silicates as hereinabove described are particularly preferred.

In addition to the silicate compound the silicate rinse solution can optionally contain a bath soluble and compatible wetting agent for enhancing contact with the passivated surface present in conventional amounts of about 0.05 up to about 5.0 g/l. The silicate rinse may also optionally include an emulsifiable organic substance such as an emulsifiable oil e.g. present in an amount of from about 1 up to about 50 g/l to provide an oily film on the non-electroplated interior surfaces of ferrous substrates to provide temporary protection against rusting during further processing steps of the parts. When such parts have surfaces which are completely passivated such as, for example, zinc die castings, the use of the optional emulsifiable oil is not necessary.

Similarly, there are applications where an oil is not desired but temporary rust protection of interior unplated surfaces is still required. In these cases a final rinse containing an alkali metal or ammonium nitrite such as sodium nitrite e.g. in an amount of about 0.1 to about 1.0 g/l may be used. In addition a wetting agent or combination of wetting agents is preferably used in conjunction with the sodium nitrite e.g. in the amounts of about 0.05 to about 5.0 g/l. The presence of silicates in the final rinse is also compatible with this treatment.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

Examples 1.1 and 1.2 relate to the first aspect of the invention which provides a chromium-like passivate through using a bath free of chromium ions.

Examples 2.1 to 2.8 relate to the second aspect of the invention which utilizes iron and cobalt as the metallic activator and also incorporates trivalent chromium to produce bright bluish passivates.

Exampes 3.1 to 3.5 relate to the third aspect of the invention which utilizes cerium as the metallic activator and again incorporates trivalent chromium but this time gives a yellow passivate similar to hexavalent chromium passivates.

Examples 4.1 to 4.3 relate to the fourth aspect of the invention which utilizes a carboxylic acid in baths of the same general types as shown in the Examples of the second and third aspects. The carboxylic acid enhances the initial hardening of the passivate.

Examples 5.1 to 5.8 relate to the fifth aspect of the invention which utilizes a bath soluble silicate in the passivate bath as well as trivalent chromium in baths of the same general types as shown in the examples of the second and fourth aspects. The silicate enhances initial hardening of the passivate and corrosion resistance.

Examples 6.1 to 6.5 relate to the sixth aspect of the invention which utilizes a mixture of citric acid and a particular phosphonic acid to inhibit loss of oxidizing agent and increase of pH during use of the baths of the types described in the second and fifth aspects.

Examples 7.1 to 7.3 relate to the seventh aspect of the invention which is a post passivation silicate rinse process which produces hardening of the passivate.

Exampl 1.1

A chromium-free passivating concentrate was prepared containing 12 g/l ammonium bifluoride, 12 g/l ferrous ammonium sulphate, 80 g/l cobalt sulphate, and 4.5% by volume of concentrated sulphuric acid. An operating bath was prepared comprising water to which 2% by volume of the foregoing passivating concentrate was add d in addition to 1.5 volume p rcent hydrog n peroxid (38% concentration). The operating path had a nominal pH of about 1.5 to about 2.0.

Test panels carrying a bright electroplated zinc deposit which had been water rinsed after the electroplating step and which were rinsed in a 5% by volume dilute nitric acid solution were immersed in the operating passivating bath for a period of 20 seconds in the pr sence of mild agitation. Thereafter the test pan ls were water rinsed and air dried. The test panels after drying were visually

inspected and were characterized as having a uniform clear bluish passivating film on the surface thereof. The operating bath had a nominal pH of about 1.5 to about 2.0.

Exampl 1.2

In order to produce a light yellow iridescent passivate film on zinc electroplated test panels, cerium ions were introduced in a test operating bath containing 2% by volume of the chromium-free passivating concentrate described in Example 1.1 2% by volume of a cerium sulphate concentrate comprising a 6% cerium sulphate ($Ce(SO_4)_2$) solution in a dilute sulphuric acid solution and 1.5% by volume of a hydrogen peroxide concentrate (38%). The normal pH of the operating bath was about 1.5 to about 2.0.

The zinc test panels after plating, water rinsing and a nitric acid dip were immersed in the test solution in the presence of mild agitation for a period of 45 seconds. The treated test panels were water rinsed and air dried. A visual inspection of the surface of the test panel revealed a substantially uniform light-yellow iridescent passivate film.

Example 2.1

An operating bath was prepared containing:

Ingredient	*Concentration g/l*
$Cr_2(SO_4)_3$	2.2
NH_4HF_2	.18
H_2SO_4	1.2
H_2O_2	5.3
$FeNH_4SO_4$*	0.25
$CoSO_4 \cdot 7H_2O$	1.6

*Ferrous Ammonium Sulphate=$Fe(SO_4) \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Steel test panels were subjected to an alkaline, non-cyanide electroplating step to deposit a zinc plating thereon after which they were thoroughly water rinsed and immersed with agitation in the above operating bath for a period of 20 seconds. At the conclusion of the treatment, the passivated panels were warm water rinsed, and air dried. An inspection of the coating on the panels after drying revealed an exceptionally bright clear-bluish colouration with no haziness. Additionally, the coating exhibited the appearance of a bright nickel chromium electroplating and also exhibited excellent smear resistance on light finger-rubbing.

Example 2.2

An operating bath was prepared containing:

Ingredient	*Concentration, g/l*
$Cr_2(SO_4)_3$	5.6
NH_4HF_2	0.4
H_2SO_4	2.7
H_2O_2	5.3
$FeNH_4SO_4$	0.58
$CoSO_4 \cdot 7H_2O$	3.75

The operating bath of Example 2.2 is similar to that of Example 2.1 with the exception that the trivalent chromium, ammonium bifluoride, sulphuric acid, iron and cobalt constituents are all at higher concentratrions. Zinc plated test panels treated with the bath of Example 2.2 produced results substantially equivalent to those obtained with the operating bath of Example 2.1.

Example 2.3

An operating bath was prepared containing:

Ingredient	*Concentration g/l*
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
H_2O_2	5.3
$F\ NH_4SO_4$	0.25
$NiNH_4SO_4$*	2.1

*Nickel Ammonium Sulphate—$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Zinc plated test panel treated with this operating bath under the same conditi ns as described in Example 2.1 were observed, after drying, to have a coating which was very bright with a clear bluish colouration and no haziness. The coating also exhibited good smear resistance on light finger rubbing.

Example 2.4

An operating bath was prepared identical to that as set forth in Example 2.3 with the exception that 1.6 g/l of nickel sulphate was employed in place of 2.1 g/l of nickel ammonium sulphate. The zinc plated test panels treated in the manner as previously described in Example 2.1 employing the treating solution of Example 2.4 produced results substantially comparable to those obtained with the treating bath of Example 2.3 except that the coating had a slightly less bluish colouration.

Examples 2.5A to 2.5E

A series of passivating solutions were prepared for treating zinc plated steel test panels to evaluate their relative corrosion resistance to a 5 percent neutral salt spray after passivation. The composition of the solutions 5A, 5B, 5C and 5D are given in Table 1 below:

Table 1

	Concentration, g/l			
Ingredient	*2.5A*	*2.5B*	*2.5C*	*2.5D*
$Cr_2(SO_4)_3$	3.0	3.0	3.0	3.0
NH_4HF_2	0.24	0.24	0.24	0.24
H_2SO_4	1.54	1.54	1.54	1.54
H_2O_2	5.3	5.3	5.3	5.3
$FeNH_4SO_4$	—	0.25	0.25	0.25
$CoSO_3$	—	—	1.6	—
$NiNH_4SO_4$	—	—	—	2.1

Solution 2.5A contains only trivalent chromium ions; solution 2.5B additionally contains ferrous ions; solution 2.5C contains a combination of iron and cobalt ions while solution 2.5D contains a combination of iron and nickel ions.

In addition to the foregoing operating solutions, a traditional hexavalent chromium passivating solution (Example 2.5E) was prepared to serve as a control containing 0.63 g/l sodium dichromate, 0.63 g/l ammonium bifluoride, 0.01 g/l sulphuric acid, 0.65 g/l nitric acid. This solution is designated as solution 2.5E.

Duplicate sets of 3 inch by 4 inch (7.6 cms by 10.2 cms) steel panels were cleaned and zinc plated using a non-cyanide zinc plating electrolyte for fifteen minutes at a plating current density of 20 amperes per square foot (ASF) (2.2 Amperes per Square decimetre (ASD)) whereafter they were thoroughly rinsed. Each set of zinc plated test panels was then immersed in the respective treating solution for a period of twenty seconds whereafter they were warm water rinsed, air-dried and thereafter allowed to age twenty-four hours prior to salt spray testing in accordance with ASTM standards. The test panels were subjected to the five percent neutral salt spray for a total of forty-three hours. For further comparative purposes, a duplicate set of zinc test panels without any passivation treatment was also subjected to the neutral salt spray test. The results are set forth in Table 1.

Table 1
Neutral salt spray test results

Example	*Test Panel*	*Percent White Corrosion, %*	*Percent Red Rust, %*
2.5F	Untreated	50	50%
2.5A	5A	45—55	0
2.5B	5B	10—15	0
2.5C	5C	less than 2	0
2.5D	5D	less than 10	0
2.5E	5E	45—55	0

Based on the foregoing test results it is apparent that the untreated zinc plated test panel is a gross failure; the test panel treated with solution 2.5A is a failure; the test panels treated with solution 2.5B are a marginal pass; the test panels treated with solutions 2.5C and 2.5D pass the test; and the test panel treated with solution 2.5E is a failure.

Exampl 2.6

An operating bath was prepared containing:

Ingredient	Concentration, g/l
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$MnSO_4 \cdot H_2O$	1.0

Electroplated zinc test panels prepared in accordance with the procedure as set forth in Example 2.5 were immersed in the bath of Example 2.6 for a period of 30 seconds, warm water rinsed, air dried and allowed to age 24 hours prior to 5 percent neutral salt spray testing. For comparative purposes, zinc test panels were treated with the solutions 2.5A and 2.5E of Example 2.5 and subjected to the same salt spray evaluation.

After 48 hour salt spray, an inspection of the several test panels revealed that the panels treated with the solution of Example 2.6 had superior corrosion resistance to that of the panels treated with solutions 5A and 5E.

Example 2.7

An operating bath was prepared containing:

Ingredient	Concentration, g/l
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$H_2MoO_4 \cdot H_2O$	1.0

Electroplated zinc test panels prepared in accordance with Example 2.5 were immersed in the bath of Example 2.7 for a period of 30 seconds, warm water rinsed, air dried and allowed to age for 24 hours prior to 5 percent neutral salt spray testing. For comparative purposes, zinc test panels were treated with the solutions 2.5A and 2.5E of Example 2.5 and subjected to the same salt spray evaluation.

After 48 hours of salt spray test, an inspection of the panels revealed that the panels treated with the solution of Example 2.7 had superior corrosion resistance to that of the test panels treated with solutions 2.5A and 2.5E.

Example 2.8

An operating bath was prepared containing:

Ingredient	Concentration, g/l
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$(NH_4)_4(NiMoO_{24}H_6)_4 \cdot 4H_2O$	1.0

Electroplated zinc test panels prepared in accordance with the procedure described in Example 2.5 were immersed in the bath of Example 2.8 for a p riod of 30 seconds, warm water rinsed, air dried and allow d to age for 24 hours prior to a 5 percent neutral salt spray test. For comparative purposes, zinc test panels were treated with the solutions 2.5A and 2.5E of Example 2.5 and subjected to the same salt spray evaluation.

After 48 hours salt spray, an inspection of the panels revealed that the panels treated with the solution of Example 2.8 had superior corrosion resistance in comparison to the panels treated with solutions 2.5A and 2.5E.

A relative comparison of the test panels prepared in accordance with Examples 2.6, 2.7 and 2.8 revealed that the solution of Example 2.6 containing iron ions and Molybdic acid and the solution of Example 2.8 containing iron ions in combination with ammonium 6-molybdonickelate possessed superior corrosion resistance to the test panels treated with the operating solution of Example 2.6 containing iron ions in combination with manganese ions. The test panels treated in accordance with Examples 2.7 and 2.8 also possessed superior corrosion resistance to test panels treated with the test solution 2.5B of Example 2.5 containing only iron ions whereas the test panels treated with the solution of Example 2.6 containing both iron and manganese ions possessed corrosion resistance somewhat comparable to that of panels treated with solution 2.5B.

Example 3.1

A concentrate 3.1A was prepared comprising an aqueous acidic solution containing 25 g/l trivalent chromium ions introduced as chromium sulphate (Korean MF from Allied Chemical Company), 12 g/l ammonium chloride, 12 g/l ferrous ammonium sulphate and 4% by volume of concentrated sulphuric acid.

A second aqueous acidic concentrate 3.1B was prepared containing 60 g/l tetravalent cerium ions introduced as $Ce(SO_4)_2 \cdot 4H_2O$ and 5% by volume concentrated sulphuric acid.

An operating bath was prepared comprising water containing 2% by volume concentrate 3.1A, 2% by volume concentrate 3.1B and 1.5% by volume of a 38% solution of hydrogen peroxide. Electroplated zinc test panels immersed in this operating bath for 40 to 60 seconds had light-yellow iridescent passivate films on the surfaces thereof.

Example 3.2

A concentrate 3.2A was prepared similar to concentrate 1A of Example 1 containing 25 g/l trivalent chromium ions, 20 g/l sodium chloride, 40 g/l ferric sulphate and 4% by volume concentrated sulphuric acid.

An operating bath was prepared comprising water containing 2% by volume concentrate 3.2A, 2% by volume concentrate 3.1B of Example 3.1 and from 1.5—3% by volume of a 38% solution of hydrogen peroxide. Electroplated zinc test panels immersed in the operating bath produced results similar to Example 3.1.

Example 3.3

A concentrate 3.3A was prepared similar to concentrate 3.1A of Example 3.1 except that 6% by volume nitric acid was employed in place of 4% sulphuric acid.

An operating bath was prepared comprising water containing 2% by volume concentrate 3.3A, 2% by volume concentrate 3.1B of Example 3.1 and 1.5—3% by volume of a 38% solution of hydrogen peroxide. Electroplated zinc test panels immersed in the operating bath produced results similar to Example 3.1.

Example 3.4

A concentrate 3.4A was prepared similar to concentrate 3.2A of Example 3.2 except that 6% by volume nitric acid was employed in place of 4% by volume sulphuric acid.

An operating bath was prepared comprising water containing 2% by volume concentrate 3.4A, 2% by volume concentrate 3.1B of Example 3.1 and 1.5—3% by volume of a 38% solution of hydrogen peroxide. Electroplated zinc test panels immersed in the operating bath produced results similar to Example 3.1.

Examples 3.5A to 3.5G

A series of seven aqueous test solutions were prepared each containing 1 g/l trivalent chromium ions, 1 g/l nitric acid, 1 g/l sulphuric acid, 7 g/l hydrogen peroxide and having a nominal pH of about 1.5. To each test solution controlled additions of metal ions were made to evaluate the effect of such additions on the colour, hardness and salt spray resistance of the passivate films produced on electroplated zinc test panels immersed in each test operating bath in the presence of mild agitation for a period of about 30 seconds and at a temperature of about 70°F (21°C).

The cerium ions were introduced as a $CeCl_3$ solution containing about 300 g/l cerium ions; the manganese ions were introduced as $MnSO_4 \cdot H_2O$; the ferric ions were introduced as $Fe_2(SO_4)_3$ dissolved in a dilute sulphuric acid solution, the molybdenum ions were introduced as sodium molybdate dry salt; the lanthanum ions were introduced as an $LaCl_3$ solution containing about 85 g/l lanthanum ions; and the cobalt ions were introduced as cobalt sulphate. The test solutions are designated as Examples 3.5A to 3.5G and the concentration of metal ion additions are summarised in Table 2.

Tabl 2
Metal ion conc ntration g/l

Metal ion	Example 3.5A	3.5B	3.5C	3.5D	3.5E	3.5F	3.5G
Cr^{+3}	1	1	1	1	1	1	1
Ce^{+3}	2	2	2	2	2	2	2
Mn^{+2}	—	0.9	—	—	—	—	—
Fe^{+3}	—	—	0.22	—	—	0.08	0.08
Mo^{+6}	—	—	—	1.0	—	—	—
La^{+3}	—	—	—	—	1.0	—	—
Co^{+2}	—	—	—	—	—	—	0.13

Each test panel after immersion in the test operating bath was water rinsed and air dried and was visually inspected for colour and clarity. All of the test panels treated in solutions 3.5A to 3.5G were of a substantially uniform light-yellow colour varying in clarity from a clear yellow film to films which were slightly hazy or hazy as set forth in Table 3. Each test panel after air drying was immediately tested for hardness of the passivate film by a light finger rubbing. The comparative hardness test results of the passivate film on the test panels treated in test solutions 3.5A to 3.5G is set forth in Table 3. It will be noted, that after a 24 hour aging of the test panels, the passivate film thereon became hard and rub resistant. The advantage of a passivate film which is hard immediately after air drying is that it can be handled for further processing without undergoing damage to the deposited film. Each test panel treated with test operating solutions 3.5A to 3.5G was also subjected to a neutral salt spray for a period of 72 hours and the surface area, expressed in terms of a percentage, in which a white corrosion deposit was formed is also tabulated in Table 3.

Table 3
Test results

Example	*Clarity*	*Hardness*	*Neutral Salt Spray 72 Hrs.—% White Corrosion*
3.5A	Sl. haze	Soft	50
3.5B	Sl. haze	Soft	100
3.5C	Sl. haze	Hard	10
3.5D	Haze	Hard	0
3.5E	Sl. haze	Soft	100
3.5F	Clear	Soft	2
3.5G	Clear	Hard	0

Based on the data as set forth in Table 2, from a clarity and hardness evaluation, Example 3.5G is a definite pass, Examples 3.5C and 3.5F are acceptable, which Examples 3.5A, 3.5B and 3.5E are less acceptable based on general appearance. From the standpoint of corrosion resistance, Examples 3.5D, 3.5F and 3.5G are definite passes, 3.5C a marginal pass, while Examples 3.5A, 3.5B and 3.5E are considered not acceptable based on ASTM corrosion standard specifications for a 72 hour neutral salt spray evaluation. It should be pointed out, however, that each of the test samples possess improved corrosion resistance in comparison to an untreated electroplated zinc test panel and the passivate films which failed the 72 hour neutral salt spray test are nevertheless acceptable for less rigorous service exposures. The corrosion resistance provided by the Example 3.5G is substantially comparable to that attainable with conventional prior art hexavalent chromium passivate solutions of the types heretofore known. It will also be appreciated that variations in the types, combinations and concentrations of the metal ions contained in the test solutions can be made to optimize and improve the clarity, hardness and corrosion resistance of the test panels over the results as set forth in Table 3. The selection of a 72 hour neutral salt spray condition is relatively severe and is generally employed for parts subjected to exterior exposure such as in automotive components. The 72 hour neutral salt spray test is normally applied to yellow hexavalent chromium passivates although some specifications require only 48 hours while others require a 96 hour exposure. The 72 hour test period was, accordingly, selected as being of average severity.

Exampl s 4.1A to 4.1G

A series of trivalent chromium containing concentrates were prepared suitable for dilution with water to make up an operating bath in further combination with an oxidizing agent and cerium or lanthanum ions as follows:

C ncentrate 4.1A

Ingredient	*Concentration, g/l*
Cr^{+3}	24
$CoSO_4 \cdot 7H_2O$	25
Ferrous ammonium sulphate	12
Sodium fluoroborate	15
Succinic acid	25
Nitric acid (100%)	60

Concentrate 4.1B

Ingredient	*Concentration, g/l*
Cr^{+3}	24
NaCl	20
Ferrous ammonium sulphate	25
Sodium succinate	55
Nitric acid (100%)	60

Concentrate 4.1C

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
Sodium succinate	55
NaCl	20
Nitric Acid (100%)	60

Concentrate 4.1D

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
Succinic acid	25
NaCl	20
Nitric acid (100%)	60

Concentrate 4.1E

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
NaCl	20
Malonic acid	25
Nitric acid (100%)	60

Concentrate 4.1F

Ingredient	*Concentration, g/l*
Cr^{+3}	24
$Fe_2(SO_4)_3$	30
NaCl	20
Gluconic acid	20
Nitric acid (100%)	60

Concentrate 4.1G

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
NaCl	20
Maleic acid	25
Nitric acid (100%)	60

Examples 4.2A to 4.2G

A cerium ion concentrate was provided containing about 80 g/l ceric ions in the form of ceric sulphate in a dilute sulphuric acid solution. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide. A series of operating baths were prepared suitable for forming a yellow passivate film on a substrate each containing 2% by volume of the cerium ion concentrate, 2% by volume of the oxidizing agent concentrate, and 2% by volume of one of the chromium concentrates 4.1A to 4.1 G of Examples 4.1A to 4.1G.

Steel test panels were subjected to an alkaline, non-cyanide electrplating step to deposit a zinc plating thereon after which they were thoroughly water rinsed and immersed with agitation in each of the test operating baths for a period of about 30 seconds maintained at a temperature of about 70°F (21°C) and having a pH ranging from about 1.5 to about 2.0. At the conclusion of the passivation treatment, the passivated panels were warm water rinsed and air dried. An inspection of the coating on each of the test panels which had been immersed in each of the operating test solutions revealed the formation of a clear hard yellow passivate film.

Examples 4.3A to 4.3G

A lanthanum ion concentrate was provided containing about 60 g/l lanthanum ions in the form of a solution of lanthanum chloride. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide. A series of operating baths were prepared suitable for forming a blue-bright passivate film on a substrate each containing 2% by volume of the lanthanum ion concentrate, 2% by volume of the oxidizing agent concentrate, and 2% by volume of one of the chromium concentrates 4.1A to 4.1G of Example 4.1.

Zinc plated test panels as described in Example 4.2 were immersed under the conditions described in Example 4.2 whereafter they were warm water rinsed and air dried. An inspection of the coating on each of the test panels after drying revealed an exceptionally bright, clear, hard bluish coloured passivate film.

The yellow passivated panels of Examples 4.2A, 4.2B and 4.2C produced using operating baths containing, respectively, concentrates 4.1A, 4.1B and 4.1C as hereinabove described were aged for at least 24 hours and subjected to neutral salt spray corrosion testing according to ASTM procedure B-117. The following Table 4 indicates the corrosion resistance results that were obtained using these formulations:

Table 4

Example	*Chromium Concentrate*	*Hours Neutral 72*	*Salt Spray 96*
4.2A	4.1A	Clear with some dark spots.	Clear with some dark spots.
4.2B	4.1B	Clear with some dark spots.	Clear with some dark spots.
4.2C	4.1C	Clear with some dark spots.	Some dark spots—1% white spots.

The above results show that panels treated with operating baths containing concentrates A, B, and C passed the 96 hour salt spray test. Similar results were obtained with panels produced using the other concentrat s.

Example 5.1

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a trivalent chromium containing concentrate designated as "Concentrate 5.1A" having a composition as follows:

Conc ntrat 5.1A

Ingredient	Concentration, g/l
Cr^{+3}	50
Ferric ammonium sulphate	30
Sodium chloride	20
Nitric acid (100%)	60
Succinic acid	20

The trivalent chromium ions were introduced as $Cr_2(SO_4)_3$.

A cerium ion concentrate designated as "Concentrate 5.1B" was provided containing about 80 g/l ceric ions in the form of ceric sulphate in a dilute (about 5%) sulphuric acid solution. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide. A sodium silicate concentrate was also provided containing 300 g/l sodium silicate calculated as SiO_2.

A yellow passivate operating bath was prepared comprising water containing 2% by volume of Concentrate 5.1A, 2% by volume of the cerium ion Concentrate 5.1B, 2% by volume of the oxidizing agent concentrate and 0.4% by volume of the sodium silicate concentrate.

Steel test panels were subjected to an alkaline, non-cyanide electroplating step to deposit a zinc plating thereon after which they were thoroughly water rinsed and immersed with agitation in the passivate operating bath for a period of about 30 seconds at a temperature of about 70°F (21°C) and at a pH ranging from about 1.5 to about 2.0. The test panels were thereafter extracted from the operating bath and were dried with recirculating warm air.

The test panels after drying were visually inspected and were observed to have a very hard clear yellow passivate film. The test panels after aging for at least 24 hours, were subject to a neutral salt spray corrosion test according to ASTM Procedure B-117. The test panels thus treated in accordance with the present process exhibited excellent salt spray resistance after exposure for a period of more than 96 hours.

Example 5.2

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a trivalent chromium containing concentrate designated as "Concentrate 5.2A" having a composition as follows:

Concentrate 5.2A

Ingredient	Concentration, g/l
Cr^{+3}	50
Ferric ammonium sulphate	40
Sodium chloride	20
Nitric acid (100%)	60
Sodium silicate (calculated as SiO_2)	10

A yellow passivate operating bath was prepared comprising water containing 2% by volume of Concentrate 5.2A, 2% by volume of the cerium ion Concentrate 5.1B of Example 5.1, and 2% by volume of the oxidizing agent concentrate of Example 5.1.

Test panels prepared in accordance with the procedure described in Example 5.1 were immersed in the operating bath for a period of about 30 seconds at a temperature of about 70°F (21°C) and at a pH ranging from about 1.5 to about 2.0. The treated test panels were dried with recirculating warm air and the dried panels were observed to have a very hard clear yellow passivate film. The test panels after aging were subjected to a neutral salt spray corrosion test as described in Example 5.1 and were observed to possess excellent salt spray resistance after exposure for a period of more than 96 hours.

Example 5.3

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a trivalent chromium containing concentrate designated as "Concentrate 5.3A" having a composition as follows:

Conc ntrate 5.3A

Ingredient	Concentration, g/l
Cr^{+3}	50
Ferric ammonium sulphate	40
Nitric acid (100%)	60
Sodium chloride	20

An operating bath was prepared comprising water containing 2% by volume of Concentrate 5.3A, 2% by volume of the cerium ion containing Concentrate 5.1B of Example 5.1, 2% by volume of the oxidizing agent concentrate of Example 5.1, and 0.5% by volume of the sodium silicate concentrate of Example 5.1.

Electroplated zinc test panels were treated in the operating bath in accordance with the procedure as described in Example 5.1 and after drying, were observed to have a good clear yellow passivate film.

The test panels also possessed good salt spray resistance evidencing excellent corrosion protection.

Example 5.4

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a trivalent chromium containing concentrate incorporating a quaternary amine silicate designated as "Concentrate 5.4A" having a composition as follows:

Concentrate 5.4A

Ingredient	*Concentration, g/l*
Cr^{+3}	30
Quaternary amine silicate*	15
Sodium chloride	15

*Quaram 220, calculated as SiO_2.

The trivalent chromium containing Concentrate 5.4A was subjected to prolonged storage and was observed to possess excellent stability over prolonged storage times.

In addition, a second concentrate designated as "Concentrate 5.4B" was prepared having a composition as follows:

Concentrate 5.4B

Ingredient	*Concentration, g/l*
Nitric acid (100%)	60
Sulphuric acid (100%)	30
Ferric sulphate	25
Cerium chloride	120

An operating bath was prepared comprising water containing 2% by volume of Concentrate 5.4A, 2% by volume of Concentrate 5.4B and 2% by volume of the oxidizing agent concentrate as described in Example 5.1.

Zinc plating test panels were contacted with the operating bath in accordance with the procedure and under the conditions as described in Example 5.1 whereafter the test panels were dried with recirculating warm air. The test panels were observed to have an excellent hard and clear yellow passivate film and possess excellent salt spray resistance showing zero white corrosion formation after exposure to a neutral salt spray test for a period of 96 hours.

Example 5.5

A second series of electroplated zinc test panels were treated with the operating bath as previously described in Example 5.4 under the same conditions whereafter the test panels were water rinsed and thereafter post-rinsed for a period of 30 seconds in an aqueous solution at room temperature containing 10 g/l sodium silicate calculated as SiO_2. The panels after the post rinse were extracted and dried with warm air.

The test panels were inspected and observed to possess a very hard clear yellow passivate film. After aging, the test panels were subjected to a neutral salt spray corrosion test and exhibited excellent salt spray resistance after exposure of 96 to 140 hours. These tests also showed that when a post silicate rinse treatment is employed, the presence of some nitrate ions in the passivate operating bath is desirabl to avoid the formation of some haze, in some instances, in the passivate film as a result of the post dip operation.

Example 5.6

An operating bath suitable for depositing a blue-bright passivate film on a receptive substrate was provided by forming a concentrate designated as "Concentrate 5.6A" having a composition as follows:

Concentrate 5.6A

Ingredient	*Concentration, g/l*
Nitric acid (100%)	30
Sulphuric acid (100%)	20
Succinic acid	20
La-RE-Cl_3	80

A passivate operating bath was prepared comprising water containing 3% by volume of Concentrate 5.4A of Example 5.4, 3% by volume of Concentrate 5.6A and 3% by volume of the oxidizing agent concentrate of Example 5.1.

Electroplated zinc test panels were treated with the operating bath in accordance with the procedure as previously described in Example 5.1 and the test panels after drying were observed to possess an excellent blue-bright passivate film. The test panels also possessed excellent corrosion resistance as shown by the absence of white corrosion after being subjected to a neutral salt spray corrosion test for a period of from 48 up to 72 hours.

Examples 5.7.1 and 5.7.2

A trivalent chromium containing concentrate was prepared designated as "Concentrate 5.7A" having a composition as follows:

Concentrate 5.7A

Ingredient	*Concentration, g/l*
Cr^{+3}	30
Sodium chloride	10
Sodium silicate (calculated as SiO_2)	10

An operating bath (Example 5.7.1) suitable for depositing a yellow passivate film on a receptive substrate was prepared by employing 2% by volume of Concentrate 5.7A, 2% by volume of Concentrate 5.4B of Example 5.4 and 2% by volume of the oxidizing agent concentrate of Example 5.1. On the other hand, an operating bath (Example 5.7.2) suitable for depositing a blue-bright passivate film was achieved by employing 2% by volume of Concentrate 5.7A, 2% by volume of Concentrate 5.6A of Example 5.6 and 2% by volume of the oxidizing agent concentrate of Example 5.1.

Test panels treated in accordance with the procedure described in Example 5.1 evidenced excellent passivate films and exhibited excellent corrosion protection.

Example 5.8

An operating bath suitable for depositing a blue-bright passivate film on a receptive substrate was provided by forming a trivalent chromium containing concentrate designated as "Concentrate 5.8A" having a composition as follows:

Concentrate 5.8A

Ingredient	*Concentration, g/l*
Cr^{+3}	30
Sodium chloride	13
Sodium gluconate	10
Quaternary amine silicate*	15

*Quaram 220, calculated as SiO_2

A second concentrate designated as "Concentrate 5.8B" was provided having a composition as follows:

C nc ntrate 5.8B

Ingredient	*Concentration, g/l*
Nitric acid (100%)	60
Sulphuric acid (100%)	30
$Al_2(SO_4)_3$	30

An operating bath was prepared comprising water containing 3% by volume of Concentrate 5.8A, 3% by volume of Concentrate 5.8B and 3% by volume of the oxidizing agent concentrate of Example 5.1.

Electroplated zinc test panels were treated in accordance with the procedure described in Example 5.1 and after drying were observed to have a clear bright passivate film. Testing of such panels in neutral salt spray corrosion tests evidenced a corrosion resistance of at least 12 up to 24 hours.

Example 6.1

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a trivalent chromium concentrate designated as "Concentrate 6.1A" having a composition as follows:

Concentrate 6.1A

Ingredient	*Concentration, g/l*
Cr^{+3}	30
Quaternary ammonium silicate	15
NaCl	15

The trivalent chromium ions were introduced as $Cr_2(SO_4)_3$ while the silicate compound was introduced as Quram 220 from Emergy Industries.

A cerium ion concentrate designated as "Concentrate 6.1B" was provided having a composition as follows:

Concentrate 6.1B

Ingredient	*Concentration, g/l*
HNO_3 (100%)	60
H_2SO_4 (100%)	30
$Fe_2(SO_4)_3$	25
Ce^{+3}	120

The cerium ions were introduced by way of a cerium chloride solution containing about 300 g/l Ce^{+3} ions.

In addition, an oxidizing agent concentrate was provided containing about 35% hydrogen peroxide.

A series of one litre operating baths were prepared comprising 3% by volume Concentrate 6.1A, 3% by volume Concentrate 6.1B and 3% by volume of the oxidizing agent concentrate. In order to simulate an aged operating bath used for passivation of zinc workpieces, 1 g/l of zinc dust was dissolved in each test solution.

One such test solution without further additions was designated as test solution 6.1.1 and served as the control sample. To a second test solution designated as 6.1.2, 1 g/l of citric acid and 0.4 g/l of 1-hydroxy ethylidene-1,1 diphosphonate (Dequest 2010) was added as a stabilizing agent. To a third test solution designated as 6.1.3, 1 g/l of citric acid and 0.08 g/l of 1-hydroxy ethylidene-1,1 diphosphonate (Dequest 2010) was added.

Each test solution was subjected to agitation at room temperature to simulate typical commercial practice. The pH at start and finish and the peroxide concentration measured in terms of volume percent of 35% hydrogen peroxide concentrate remaining in the bath was analyzed over a one-day period. The results are as follows:

Hydrogen peroxide concentration and pH
Test sample

Example	*6.1.1*		*6.1.2*		*6.1.3*	
Time	H_2O_2	*pH*	H_2O_2	*pH*	H_2O_2	*pH*
Start	2.56%	1.6	2.95%	1.6	3.05%	1.4
After 3.5 hours	2.39%	—	2.92%	—	2.84%	—
After 21 hours	0.83%	—	1.72%	—	2.37	1.7
After 26 hours	0.50%	2.5	1.42%	1.8	—	—

From the results as set forth in the foregoing table, it is apparent that control sample 6.1.1 devoid of any stabilizing agent rapidly lost the peroxide oxidizing agent which should be present at a concentration of at least 2% by volume to maintain proper passivation treatment. An almost complete replenishment of the oxidizing agent in Sample 6.1.1 would therefore be necessary after a period of about one day. In contrast, sample 6.1.3 exhibited only a small loss of peroxide after 21 hours while sample 6.1.2 containing a lesser quantity of Dequest 2010 in combination with 1 g/l of citric acid also exhibited a surprising superiority in peroxide stability over the control sample 6.1.1.

The stabilization of pH is also evident from the data set forth in the foregoing table. Control sample 6.1.1 rose to a pH level of 2.5 after 26 hours which would have necessitated the addition of acid to the operating bath to maintain the pH within the preferred operating range of 1.5 to 2.0. On the other hand, both samples 6.1.2 and 6.1.3 were substantially stable and remained within optimum pH range over the test duration.

Example 6.2

An aqueous stabilizer concentrate was prepared containing 570 g/l citric acid and 110 g/l 1-hydroxy ethylidene-1,1-diphosphonate (Dequest 2010). These operating solutions were prepared as described in Example 6.1 containing 3% by volume Concentrate 6.1A, 3% by volume Concentrate 6.1B, 3% by volume of the oxidizing concentrate and 1 g/l zinc dust for aging the baths. A control sample designated 6.2.1 devoid of any stabilizing agent had an initial peroxide concentration of 3% but after standing for a period of 18 hours under the conditions of Example 6.1 had a residual peroxide concentration of only 1.05% necessitating replenishment. A second test solution designated as 6.2.2 was stabilized by the addition of 2.5 millilitres/litre of the stabilizer concentrate and had an initial peroxide concentration of 3% and after a period of 18 hours had a residual peroxide concentration of 2.43 percent.

Example 6.3

In order to evaluate the effectiveness of the peroxide and pH stabilizing agent of this aspect of the present invention under actual commercial operation, the stabilizer concentrate as defined in Example 6.2 was employed for stabilizing a trivalent chromium passivate solution of a composition similar to the operating bath of Example 6.1 containing trivalent chromium ions, iron and cerium ions to provide a pH within the range of about 1.5 to about 2.0 at a temperature of about 70°F (21°C) and containing hydrogen peroxide as the oxidizing agent. Under normal operation, in the absence of the stabilizer agent, the commercial operating bath necessitated a replenishment of the peroxide oxidizing agent with the addition of 3% by volume of a 35% hydrogen peroxide concentrate each morning at the commencement of operation as well as the addition of another 1% by volume of the peroxide oxidizing concentrate after about 4 hours operation to maintain the bath at a minimum of 2% by volume oxidizing agent.

By the addition of 1 litre of the stabilizer concentrate per one hundred gallons of the operating bath, the replenishment of the peroxide oxidizing concentrate was reduced to only a 1% by volume replenishment each operating day and only a 2% by volume replenishment after standing over the weekend to restore the bath to a proper operating condition.

Additionally, the addition of the stabilizer concentrate to the operating bath further stabilized the operating pH over the six day test period wherein the pH remained substantially constant avoiding the necessity of acid addition to control pH. In contrast, the same commercial operating bath without any of the stabilizer concentrate necessitated frequent monitoring of pH and periodic addition of acid to maintain the pH within the desired range of 1.5 to 2.0.

Bright zinc electroplated parts processed employing the foregoing commercial operating bath after aging for at least 24 hours were subjected to a neutral salt spray corrosion test according to ASTM Procedure B-117. The excellent corrosion resistance of the yellow passivate film was evidenced by the absence of white corrosion on the parts after 96 hours salt spray testing.

Example 6.4

The stabilization of a commercial operating bath of a composition and employing the procedure as described in Example 6.3 was achieved by preparing an aqueous stabilizer concentrate containing from about 30 to about 170 g/l of 1-hydroxy ethylidene-1,1 diphosphonate (Dequest 2010) in admixture with about 160 to about 500 g/l of citric acid. The stabilizing concentrat was added to the commercial operating bath to provide an operating concentration of the 1-hydroxy ethylidene-1,1 diphosphonate in an amount of about 0.05 to about 3 g/l and an operating concentration of the citric acid constituent of about 0.1 to about 10 g/l. Results obtained are similar to those as described in Example 6.3.

Exampl 6.5

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was provided by forming a concentrate designated as "Concentrate 6.5A" having a composition as follows:

Concentrat 6.5A

Ingredient	*Concentration, g/l*
HNO_3 (100%)	60
H_2SO_4 (100%)	30
$Fe_2(SO_4)_3$	25
$FeCl_3$	5
Diphosphonate*	8.5
Citric acid	36
Ce^{+3}	120

*Dequest 2010

An operating bath was prepared comprising 3% by volume of the chromium ion concentrate 6.1A of Example 6.1, 3% by volume of concentrate 6.5A and 3% by volume of the oxidizing agent concentrate containing about 35% hydrogen peroxide.

Steel test panels were subjected to an alkaline non-cyanide electroplating step to deposit a zinc plating thereon after which they were thoroughly water rinsed and immersed with agitation in the passivate operating bath for a period of about 30 seconds at a temperature of about 70°F (21°C) and at a pH ranging from about 1.5 to about 2.0. The test panels were thereafter extracted from the operating bath and were dried with recirculating warm air.

The test panels after drying were visually inspected and were observed to have a uniform clear yellow passivate film thereover. The small addition of ferric chloride to the operating bath provides an improvement in the colour intensity of the yellow passivate film in comparison to that obtained employing the passivate operating bath of Example 6.1.

The test panels after aging were subjected to a neutral salt spray test in accordance with the procedure described in Example 6.3 and similar results were obtained.

Example 7.1

An operating bath suitable for depositing a yellow passivate film on a receptive substrate was made up as follows: A trivalent chromium containing concentrate designated as "Concentrate 7.1A" having a composition was first made up as follows:

Concentrate 7.1A

Ingredient	*Concentration, g/l*
Cr^{+3}	25
Ferric ammonium sulphate	30
Sodium chloride	20
Nitric acid (100%)	60
Succinic acid	20

A cerium ion concentrate 7.1B was provided containing about 80 g/l ceric ions in the form of ceric sulphate in a dilute (about 5%) sulphuric acid solution. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide.

A yellow passivate operating bath was prepared comprising water containing 2% by volume of Concentrate 7.1A, 2% by volume of the cerium ion concentrate 7.1B and 2% by volume of the oxidizing agent concentrate 7.1C.

An aqueous silicate rinse solution was provided containing 10 g/l sodium silicate calculated as SiO_2.

Steel tests panels were subjected to an alkaline, non-cyanide electroplating step to deposit a zinc plating thereon after which they were thoroughly water rinsed and immersed with agitation in the passivate operating bath for a period of about 30 seconds at a temperature of about 70°F (21°C) and at a pH ranging from about 1.5 to about 2.0. The test panels were extracted from the operating bath, subjected to a tap water rinse and were thereafter contacted with the silicate rinse solution for about 30 seconds at a temperature of about 70°F (21°C). The silicate rinsed test panels were thereafter extracted from the rinse solution and were dried with recirculating warm air.

The test panels after drying were visually inspected and were observed to have a very hard clear yellow passivate film. The test panels after aging for at least 24 hours, were subjected to a neutral salt spray corrosion test according to ASTM Procedure B-117. The test panels treated in accordance with the present process exhibited excellent salt spray resistance after exposure for a period of more than 96 hours.

Examples 7.2.1 to 7.2.14

A series of trivalent chromium containing concentrates was prepared suitable for dilution with water to make up an operating bath in further combination with an oxidizing agent and cerium or lanthanum ions as follows:

Concentrate 7.2A

Ingredient	*Concentration, g/l*
Cr^{+3}	24
$CoSO_4 \cdot 7H_2O$	25
Ferrous ammonium sulphate	12
Sodium fluoroborate	15
Succinic acid	25
Nitric acid (100%)	60

Concentrate 7.2B

Ingredient	*Concentration, g/l*
Cr^{+3}	24
NaCl	20
Ferrous ammonium sulphate	25
Sodium succinate	55
Nitric acid (100%)	60

Concentrate 7.2C

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
Sodium succinate	55
NaCl	20
Nitric acid (100%)	60

Concentrate 7.2D

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
Succinic acid	25
NaCl	20
Nitric acid (100%)	60

Concentrate 7.2E

Ingredient	*Concentration, g/l*
Cr^{+3}	24
Ferric ammonium sulphate	50
NaCl	20
Malonic acid	25
Nitric acid (100%)	60

Concentrate 7.2F

Ingredient	*Concentration, g/l*
Cr^{+3}	24
$Fe_2(SO_4)_3$	30
NaCl	20
Gluconic acid	20
Nitric acid (100%)	60

Conc ntrate 7.2G

Ingredient	Concentration, g/l
Cr^{+3}	24
Ferric ammonium sulphate	50
NaCl	20
Maleic acid	25
Nitric acid (100%)	60

A cerium ion concentrate was provided containing about 80 g/l ceric ions in the form of ceric sulphate in a dilute sulphuric acid solution. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide. A series of operating baths (Examples 7.2.1 to 7.2.7) were prepared suitable for forming a yellow passivate film on a substrate each containing 2% by volume of the cerium ion concentrate, 2% by volume of the oxidizing agent concentrate, and 2% by volume of one of the chromium concentrates 7.2A to 7.2G respectively.

A lanthanum ion concentrate was provided containing about 60 g/l lanthanum ions in the form of a solution of lanthanum chloride. An oxidizing agent concentrate was also provided containing about 35% hydrogen peroxide. A series of operating baths (Examples 7.2.8 to 7.2.14) were prepared suitable for forming a blue-bright passivate film on a substrate each containing 2% by volume of the lanthanum ion concentrate, 2% by volume of the oxidizing agent concentrate, and 2% by volume of one of the chromium concentrates 7.2A to 7.2G respectively.

Zinc plated steel test panels as described in Example 7.1 were processed through each of the operating baths (Examples 7.2.1 to 7.2.14) under the conditions as set forth in Example 7.1 whereafter the passivated panels were subjected to a silicate post-rinse treatment employing an aqueous silicate rinse solution in which the silicate concentration was varied from about 1 to about 40 g/l calculated as SiO_2 at temperatures ranging from 50° to 150°F (10° to 66°C). The panels were subsequently air dried and subjected to a neutral salt spray corrosion test as described in Example 7.1. Similar results to those reported for Example 7.1 were obtained.

Examples 7.3.1 to 7.3.6

A series of operating baths was prepared as follows:

Operating bath 7.3A

Ingredient	Concentration, g/l
$Cr_2(SO_4)_3$	2.2
NH_4HF_2	.18
H_2SO_4	1.2
H_2O_2	5.3
$FeNH_4SO_4$*	0.25
$CoSO_4 \cdot 7H_2O$	1.6

*Ferrous Ammonium Sulphate=$Fe(SO_4) \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Operating bath 7.3B

Ingredient	Concentration, g/l
$Cr_2(SO_4)_3$	5.6
NH_4HF_2	0.4
H_2SO_4	2.7
H_2O_2	5.3
$FeNH_4SO_4$	0.58
$CoSO_4 \cdot 7H_2O$	3.75

Operating bath 7.3C

Ingredient	*Concentration, g/l*
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
H_2O_2	5.3
$FeNH_4SO_4$	0.25
$NiNH_4SO_4$*	2.1

*Nickel Ammonium Sulphate=$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Operating bath 7.3D

Ingredient	*Concentration, g/l*
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$MnSO_4 \cdot H_2O$	1.0

Operating bath 7.3E

Ingredient	*Concentration, g/l*
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$H_2MoO_4 \cdot H_2O$	1.0

Operating bath 7.3F

Ingredient	*Concentration, g/l*
$Cr_2(SO_4)_3$	3.0
NH_4HF_2	0.24
H_2SO_4	1.54
$FeNH_4SO_4$	0.24
H_2O_2	5.3
$(NH_4)_4(NiMoO_{24}H_6)_4 \cdot 4H_2O$	1.0

Zinc plated test panels prepared as previously described in Example 1 were processed through the foregoing operating baths (Examples 7.3.1 to 7.3.6) under the conditions previously described in Example 7.1 whereafter they were water rinsed and subjected to an aqueous silicate post-rinse treatment in a rinse solution in which the silicate concentration calculated as SiO_2 was varied from about 1 to about 40 g/l at temperatures ranging from about 50° to about 150°F (10° to 66°C). The passivated and post rinsed panels after drying were subjected to salt spray tests as described in Example 7.1 and similar results were obtained.

Claims

1. An aqueous acidic solution useful in the treatment of receptive metal substrates to impart a passivate film thereon comprising

A) hydrogen ions to provide an acidic pH,

B) an oxidizing agent, and

C) at least one of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture or cerium ions or mixtures thereof in an amount effective to impart increased corrosion resistance to the treated substrate.

2. An aqueous acidic solution of treating receptive metal substrates to impart a passivate film thereon comprising

A) an acid,

B) an oxidizing agent, and

C) iron and cobalt ions present in an amount effective to impart increased corrosion resistance to the treated substrate.

3. An aqueous solution as claimed in Claim 1 or claim 2 also comprising

D) chromium ions substantially all of which are in the trivalent state.

4. An aqueous acidic solution for treating receptive metal substrates to impart a chromate passivate film thereon comprising

A) an acid,

B) an oxidizing agent,

C) iron ions in combination with at least one additional metal ion selected from the group consisting of cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture and mixtures thereof present in an amount effective to impart increased corrosion resistance to the treated substrate, and

D) chromium ions substantially all of which are in the trivalent state.

5. An aqueous acidic solution for treating receptive metal substrates to impart a chromate passivate film thereon comprising

A) an acid,

B) an oxidizing agent,

C) cerium ions present in an amount effective to impart increased corrosion resistance to the treated substrate, and

D) chromium ions substantially all of which are in the trivalent state.

6. An aqueous acidic solution for treating receptive metal substrates to impart a chromate passivate film thereon comprising

A) hydrogen ions to provide an acidic pH,

B) an oxidizing agent,

C) at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture and cerium and mixtures thereof present in an amount effective to impart increased corrosion resistance to the treated substrate,

D) chromium ions substantially all of which are in the trivalent state, and

E) a bath soluble and compatible organic carboxylic acid present in an amount effective to impart initial hardness and clarity to the passivate film, the said organic acid having the structural formula:

$$(OH)_aR(COOH)_b$$

wherein:

a is an integer from 0 to 6;

b is an integer from 1 to 3; and

R represents an alkyl, alkenyl, or aryl group containing from C_1 to C_6 carbon atoms;

as well as the bath soluble and compatible salts thereof.

7. An aqueous acidic solution for treating receptive metal substrates to impart a chromate passivate film thereon comprising

A) hydrogen ions to provide an acidic pH,

B) an oxidizing agent,

C) at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture and cerium and mixtures thereof present in an amount effective to impart increased corrosion resistance to the treated substrate,

D) chromium ions substantially all of which are present in the trivalent state and present in an amount effective to produce a chromate film, and

F) a bath soluble and compatible silicate compound present in an amount effective to provide improved hardness to the passivate film, and improved corrosion protection to the substrate.

8. An aqueous acidic solution for treating receptive metal substrates to impart a chromate passivate film thereon comprising

A) hydrogen ions to provide an acidic pH,

B) an oxidizing agent,

C) at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture and cerium and mixtures thereof present in an amount effective to impart increased corrosion resistance to the treated substrate.

D) chromium ions substantially all of which are present in the trivalent state and present in an amount effective to produce a chromate film, and

G) a stabilizing agent comprising a mixture of 1-hydroxy ethylidene-1,1 diphosphonic acid and citric acid as well as the bath soluble and compatible salts thereof present in an amount effective to reduce loss of the oxidizing agent and to inhibit a rise in the pH of the solution.

9. An aqueous acidic solution as claimed in anyone of claims 1 to 8 in which ingredient A is provided by an acid.

10. An aqueous solution as claimed in claim 9 in which the said acid is a mineral acid.

11. An aqueous solution as claimed in claim 10 in which the mineral acid comprises sulphuric, nitric or hydrochloric acid or mixtures thereof.

12. An aqueous solution as claimed in anyone of claims 1 to 11 having a pH of about 1.2 to about 2.5.

13. An aqueous solution as claimed in anyone of claims 1 to 12 having a pH of about 1.5 to about 2.2.

14. An aqueous solution as claimed in anyone of claims 1 to 13 having a pH of about 1.5 to about 2.0.

15. An aqueous solution as claimed in anyone of claims 1 to 14 having a pH of about 1.6 to about 1.8.

16. An aqueous solution as claimed in anyone of claims 1 to 15 in which the said oxidizing agent, ingredient B, is present in an amount of about 1 to 20 g/l calculated on a weight equivalent effectiveness basis to hydrogen peroxide.

17. An aqueous solution as claimed in claim 16 in which the said oxidizing agent is present in an amount of about 3 to about 7 g/l calculated on a weight equivalent effectiveness basis to hydrogen peroxide.

18. An aqueous solution as claimed in anyone of claims 1 to 17 in which the said oxidizing agent comprises a peroxide.

19. An aqueous solution as claimed in claim 18 in which the said oxidizing agent comprises hydrogen peroxide.

20. A process as claimed in anyone of claims 1 to 19 in which the said at least one additional metal ion in the said aqueous acidic solution is present in an amount up to about 10 g/l e.g. in the range of about 0.5 to about 10 g/l.

21. An aqueous solution as claimed in anyone of claims 15 to 20 in which ingredient C is present in an amount up to about 1 g/l.

22. An aqueous solution as claimed in Claim 21 in which ingredient C is present in an amount of about 0.02 to about 1 g/l.

23. An aqueous solution as claimed in claim 22 in which ingredient C is present in an amount of about 0.1 to about 0.2 g/l.

24. An aqueous solution as claimed in anyone of claims 1 to 23 further containing at least one additional metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, lanthanum, lanthanide mixture as well as mixtures thereof.

25. An aqueous solution as claimed in anyone of claims 1 to 24 further containing as an additional metal ion aluminium.

26. An aqueous solution as claimed in claim 25 in which the said at least one additional metal ion comprises iron.

27. An aqueous solution as claimed in anyone of claims 24, 25 or 26 in which the said at least one additional metal ion comprises cobalt.

28. An aqueous solution as claimed in anyone of claims 24 to 27 in which the said at least one additional metal ion comprises nickel.

29. An aqueous solution as claimed in anyone of claims 24 to 28 in which the said at least one additional metal ion comprises molybdenum.

30. An aqueous solution as claimed in anyone of claims 24 to 29 in which the said at least one additional metal ion comprises manganese.

31. An aqueous solution as claimed in anyone of claims 24 to 30 in which the said at least one additional metal ion comprises lanthanum.

32. An aqueous solution as claimed in anyone of claims 24 to 31 in which the said at least one additional metal ion comprises lanthanide mixture.

33. An aqueous solution as claimed in anyone of claims 24 to 32 in which the said at least one additional metal ion comprises aluminium.

34. An aqueous solution as claimed in anyone of claims 1 to 33 in which the trivalent chromium ions, ingr dient D, are present in an amount of about 0.05 g/l up to saturation.

35. An aqueous solution as claimed in claim 34 in which the trivalent chromium ions are present in an amount of about 0.2 to about 2 g/l.

36. An aqueous solution as claimed in claim 35 in which the trivalent chromium ions are present in an amount of about 0.5 to about 1 g/l.

37. An aqueous solution as claimed in anyone of claims 1 to 36 further including halide ions.

38. An aqueous solution as claimed in claim 37 in which the said halide ions are present in an amount up to about 8 g/l.

39. An aqueous solution af claimed in claim 38 in which the said halide ions are present in an amount of about 0.1 to about 2.5 g/l.

40. An aqueous solution as claimed in claim 37 in which the said halide ions are present in an amount up to about 2 g/l.

41. An aqueous solution as claimed in claim 40 in which the said halide ions are present in an amount of about 0.1 to 0.5 g/l.

42. An aqueous solution as claimed in anyone of claims 1 to 41 further containing a surfactant.

43. An aqueous solution as claimed in claim 42 in which the said surfactant is present in an amount up to about 1 g/l.

44. An aqueous solution as claimed in claim 43 in which the said surfactant is present in an amount of about 50 to about 100 mg/l.

45. An aqueous solution as claimed in anyone of claims 1 to 44 further containing sulphate ions in an amount up to about 15 g/l.

46. An aqueous solution as claimed in claim 45 containing sulphate ions in an amount of about 0.5 to about 5 g/l.

47. An aqueous solution as claimed in claim 4 or as claimed in anyone of claims 9 to 46 when appendant to claim 4 in which the said iron ions are present in an amount of about 0.05 to about 0.5 g/l.

48. An aqueous solution as claimed in claim 47 in which the said iron ions are present in an amount of about 0.1 to about 0.2 g/l.

49. An aqueous solution as claimed in claim 2 or as claimed in anyone of claims 9 to 48 when appendant to claim 2 in which the said iron and the said cobalt ions are present in an amount of about 0.02 to about 1 g/l.

50. An aqueous solution as claimed in claim 49 in which the said iron and the said cobalt ions are present in an amount of about 0.1 to about 0.2 g/l.

51. An aqueous solution as claimed in anyone of claims 2, 3 or 4 or claims 6 to 50 when appendant to claims 2, 3 or 4 further containing cerium ions present in an amount of about 0.5 to about 10 g/l.

52. An aqueous solution as claimed in claim 51 containing cerium ions in an amount of about 1.0 to about 4 g/l.

53. An aqueous solution as claimed in claim 5 or in anyone of claims 9 to 52 when appendant to claim 5 in which the said cerium ions are present in an amount of about 0.5 to about 10 g/l.

54. An aqueous solution as claimed in claim 53 in which the said cerium ions are present in an amount of about 1.0 to about 4 g/l.

55. An aqueous acidic solution as claimed in anyone of claims 1 to 52 containing cerium ions in an amount of about 0.5 to about 10 g/l.

56. An aqueous acidic solution as claimed in claim 55 in which the aqueous acidic solution contains cerium ions in an amount of about 1 to about 4 g/l.

57. An aqueous solution as claimed in claim 6 or in anyone of claims 9 to 56 when appendant to claim 6 in which the said carboxylic acid, ingredient E, is present in an amount of about 0.05 to about 4 g/l.

58. An aqueous solution as claimed in claim 57 in which the said carboxylic acid is present in an amount of about 0.1 to about 1 g/l.

59. An aqueous solution as claimed in claim 6 or in anyone of claims 9 to 58 when appendant to claim 6 in which the said organic carboxylic acid comprises malonic, maleic, succinic, gluconic, tartaric or citric acid or mixtures thereof as well as salts thereof.

60. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises succinic acid.

61. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises malonic acid.

62. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises maleic acid.

63. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises gluconic acid.

64. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises tartaric acid.

65. An aqueous solution as claimed in claim 57 or claim 58 in which the said carboxylic acid and salts thereof comprises citric acid.

66. An aqueous solution as claimed in claim 7 or in anyone of claims 9 to 65 when appendant to claim 7 in which the said silicate compound is present in an amount of about 0.1 to about 5 g/l calculated as SiO_2.

67. An aqueous solution as claimed in claim 66 in which the said silicate compound is present in an amount of about 0.1 to about 0.5 g/l calculated as SiO_2.

68. An aqueous solution as claimed in claim 7 or in anyone of claims 9 to 67 when appendant to claim 7 in which the said silicate compound comprises an inorganic bath soluble and compatible silicate compound present in an amount up to about 2 g/l.

69. An aqueous solution as claimed in claim 68 in which the said silicate compound comprises

an alkali metal or ammonium silicate compound present in an amount up to about 2 g/l.

70. An aqueous solution as claimed in claim 7 or in anyone of claims 9 to 67 in which the said silicate compound comprises a quaternary ammonium silicate compound present in an amount of about 0.01 to about 5 g/l calculated as SiO_2.

71. An aqueous solution as claimed in claim 70 in which the said silicate compound comprises a quaternary ammonium silicate compound present in an amount of about 0.1 to about 0.5 g/l calculated as SiO_2.

72. An aqueous solution as claimed in claim 70 or claim 71 in which the said silicate compound has the following structural formula:

$$ROR'{:}xSiO_2{:}yH_2O$$

Wherein:

R represents a quaternary ammonium radical substituted with four organic radicals selected from the group consisting of alkyl, alkylene, alkanol, aryl, or alkylaryl radicals, or mixtures thereof;

R' represents R or a hydrogen atom;

x is an integer from 1 to 3, and

y is an integer from 0 to 15.

72. An aqueous acidic solution as claimed in anyone of claims 1 to 71 further containing a bath soluble compatible organic carboxylic acid or a compatible salt thereof.

73. An aqueous solution as claimed in claim 72 in which the bath soluble and compatible organic carboxylic acid is present in an amount effective to impart initial hardness and clarity to the passivate film, the organic acid having the structural formula:

$$(OH)_a\, R\, (COOH)_b$$

Wherein:

a is an integer from 0 to 6;

b is an integer from 1 to 3; and

R represents an alkyl, alkenyl, or aryl group containing from C_1 to C_6 carbon atoms; as well as the bath soluble and compatible salts thereof.

74. An aqueous solution as claimed in claim 73 in which the said carboxylic acid is present in an amount of about 0.05 to about 4 g/l.

75. An aqueous solution as claimed in claim 74 in which the said carboxylic acid is present in an amount of about 0.1 to about 1 g/l.

76. An aqueous solution as claimed in claim 73, 74 or 75 in which the said organic carboxylic acid comprises malonic, maleic, succinic, gluconic, tartaric, or citric acid or a mixture thereof as well as salts thereof.

77. An aqueous solution as claimed in claim 8 or in anyone of claims 9 to 76 when appendant to claim 8 in which the said 1-hydroxy ethylidene-1,1 diphosphonic acid, ingredient G, is present in an amount of about 0.05 to about 3 g/l.

78. An aqueous solution as claimed in claim 77 in which the said 1-hydroxy ethylidene-1,1 diphosphonic acid is present in an amount of about 0.1 to about 0.5 g/l.

79. An aqueous solution as claimed in Claim 8 or in anyone of claims 9 to 78 when appendant to claim 8 in which the said citric acid is present in an amount of about 0.1 to about 10 g/l.

80. An aqueous solution as claimed in claim 79 in which the said citric acid is present in an amount of about 0.5 to about 1.5 g/l.

81. An aqueous concentrate suitable for dilution with water and by addition of

A) hydrogen ions to provide an acidic pH,

B) an oxidizing agent and

C) at least one metal ion selected from the group consisting of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixture and cerium, and mixtures thereof to produce an operating bath suitable for treating a receptive metal substrate to impart a chromate passivate film thereon, the said concentrate comprising about 10 to about 80 g/l of chromium ions substantially all of which are present in the trivalent state and about 5 to about 50 g/l calculated as SiO_2 of an organic quaternary ammonium silicate.

82. An aqueous concentrate as claimed in claim 81 further including up to about 50 g/l of halide ions.

83. An aqueous concentrate as claimed in claim 81 or claim 82 further including a surfactant present in an amount of up t about 5 g/l.

84. An aqueous solution as claimed in claim 4 substantially as specifically described herein with reference to Examples 2.1, 2.2, 2.3, 2.4, 2.5B, 2.5C, 2.5D, 2.6, 2.7 or 2.8.

85. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 4 or as claimed in anyone of claims 9 to 80 when appendant to claim 4 or claim 84 at a temperatur of about

40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

86. A process as claimed in claim 85 substantially as specifically described h rein with reference to anyone of the accompanying Examples 2.1 to 2.4, 2.5B, 2.5C, 2.5D, 2.6, 2.7 or 2.8.

87. A receptive substrate whenever provided with a passivate by a process as claimed in claim 85 or claim 86.

88. An aqueous solution as claimed in claim 2 substantially as specifically described herein with reference to Example 1.1 or 1.2.

89. A process for treating a receptive metal substrate to impart a passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 2 or anyone of claims 9 to 80 when appendant to claim 2 or claim 88, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

90. A process as claimed in claim 89 substantially as specifically described herein with reference to Example 1.1 or 1.2.

91. A receptive substrate whenever provided with a passivate by a process as claimed in claim 89 or claim 90.

92. An aqueous solution as claimed in claim 5 substantially as specifically described herein with reference to anyone of Examples 3.1, 3.2, 3.3, 3.4 or 3.5.

93. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 5 or as claimed in anyone of claims 9 to 80 when appendant to claim 5 or claim 92 at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

94. A process as claimed in claim 93 substantially as specifically described herein with reference to anyone of the accompanying Examples 3.1, 3.2, 3.3, 3.4 or 3.5.

95. A receptive substrate whenever provided with a passivate by a process as claimed in claim 93 or claim 94.

96. An aqueous solution as claimed in claim 6 substantially as specifically described herein with reference to anyone of Examples 4.1, 4.2 or 4.3.

97. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 6 or anyone of claims 9 to 80 when appendant to claim 6 or claim 96, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

98. A process as claimed in claim 97 substantially as specifically described herein with reference to anyone of the accompanying Examples 4.1, 4.2 or 4.3.

99. A receptive substrate whenever provided with a passivate by a process as claimed in claim 97 or claim 98.

100. An aqueous solution as claimed in claim 7 substantially as specifically described herein with reference to anyone of Examples 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7 or 5.8.

101. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 7 or as claimed in anyone of claims 9 to 80 when appendant to claim 7 or claim 100, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

102. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 7 or as claimed in anyone of claims 9 to 80 when appendant to claim 7 or claim 100, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon, contacting the passivated substrate with a dilute aqueous rinse solution for a period of at least about one second containing a bath soluble and compatible silicate compound present in an amount effective to impart improved corrosion resistance and hardness to the passivate film, and thereafter drying the passivated silicate rinsed substrate.

103. A process as claimed in claim 101 or claim 102 substantially as specifically described herein with reference to anyone of the accompanying Examples 5.1 to 5.8.

104. A receptive substrate whenever provided with a passivate by a process as claimed in claim 101, 102 or 103.

105. An aqueous solution as claimed in claim 8 substantially as specifically described herein with reference to anyone of the accompanying Examples 6.1 to 6.5.

106. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 8 or as claimed in anyone of claims 9 to 80 when appendant to claim 8 r as claimed in claim 105, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time sufficient to form a passivate film thereon.

107. A process for treating a receptive metal substrate to impart a chromate passivate film thereon which comprises the steps of contacting the substrate with a solution as claimed in claim 8 or as claimed in anyone of claims 9 to 80 when appendant to claim 8 or as claimed in claim 105, at a temperature of about 40° to about 150°F (4° to 66°C) for a period of time suffici nt to form a passivate film thereon, contacting the passivated substrate with a dilute aqueous rinse solution for a

period of at least about one second containing a bath soluble and compatible silicate compound present in an amount effective to impart improved corrosion resistance and hardness to the passivate film, and thereafter drying the passivated silicate rinsed substrate.

108. A process as claimed in claim 106 or claim 107 substantially as specifically described herein with reference to anyone of the accompanying Examples 6.1 to 6.5.

109. A receptive substrate whenever provided with a passivate by a process as claimed in claim 106, 107 or 108.

110. A process for treating a receptive metal substrate to impart an improved chromate passivate film thereon which comprises the steps of providing an aqueous acidic solution containing effective amounts of chromium ions substantially all of which are in the trivalent state, hydrogen ions to provide a pH of about 1.2 to about 2.5, an oxidizing agent, and at least one of iron, cobalt, nickel, molybdenum, manganese, aluminium, lanthanum, lanthanide mixtures and cerium as well as mixtures thereof; contacting the substrate with the said aqueous acidic solution for a period of time sufficient to form a passivate film thereon, contacting for a period of at least about one second the passivated substrate with a dilute aqueous rinse solution containing a bath soluble and compatible silicate compound present in an amount effective to impart improved hardness to the passivate film and improved corrosion resistance to the substrate and thereafter drying the passivated silicate rinsed substrate.

111. A process as claimed in claim 110 including the further step of water rinsing the said passivated substrate prior to contracting the passivated substrate with the said aqueous silicate rinse solution.

112. A process as claimed in claim 111 or claim 112 in which the the said aqueous rinse solution contains from about 1 to 40 g/l of the said silicate compound calculated as SiO_2.

113. A process as claimed in claim 112 in which the said aqueous rinse solution contains from about 5 to about 15 g/l of the said silicate compound calculated as SiO_2.

114. A process as claimed in anyone of claims 110 to 113 in which the said silicate compound comprises an inorganic compound.

115. A process as claimed in claim 114 in which the said inorganic silicate compound comprises an alkali metal or ammonium silicate.

116. A process as claimed in anyone of claims 110 to 113 in which the said silicate compound comprises an organic silicate compound.

117. A process as claimed in claim 116 in which the said organic silicate compound comprises a quaternary ammonium silicate compound.

118. A process as claimed in claim 116 or claim 117 in which the said organic silicate compound has the structural formula:

$$ROR':xSiO_2:yH_2O$$

Wherein:

R represents a quaternary ammonium radical substituted with four organic radicals selected from the group consisting of alkyl, alkylene, alkanol, aryl, alkylaryl radicals or mixtures thereof;

R′ represents a hydrogen atom;

z is an integer from 1 to 3; and

y is an integer from 0 to 15.

119. A process as claimed in anyone of claims 110 to 118 in which the said aqueous rinse solution is at a temperature of about 50° to about 150°F (10° to 66°C).

120. A process as claimed in anyone of claims 110 to 119 in which the step of contacting the passivated substrate with the said aqueous rinse solution is carried out for a period of at least about one second up to about one minute.

121. A process as claimed in anyone of claims 110 to 120 in which the said rinse solution further contains from about 0.05 to about 5 g/l of a compatible wetting agent.

122. A process as claimed in anyone of claims 110 to 121 in which the said rinse solution further contains from about 1 to about 50 g/l of an emulsifiable oil.

123. A process as claimed in anyone of claims 110 to 121 in which the said rinse solution further contains an alkali metal or ammonium nitrite or mixtures thereof in an amount of about 0.1 to about 1 g/l.

124. A process as claimed in claim 110 substantially as specifically described herein with reference to anyone of the accompanying Examples 7.1, 7.2A to 7.2N, or 7.3A to 7.3F.

125. A receptive substrate whenever subjected to a process as claimed in anyone of claims 110 to 124.

126. A r ceptiv substrate as claimed in Claim 87, 91, 95, 99, 104, 109 or 125 in which the surface treated comprises zinc, zinc alloy, cadmium, cadmium alloy, aluminium, aluminium alloy, magnesium or magnesium alloy.

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